



Computational Chemistry-Based Enthalpy-of-Formation, Enthalpy-of-Vaporization, and Enthalpy-of-Sublimation Predictions for Azide-Functionalized Compounds

by Michael J. McQuaid and Betsy M. Rice

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14. ABSTRACT <p>The applicability of semi-empirical models for estimating the gas-phase enthalpies-of-formation [$\Delta_f H_g^0(298)$], enthalpies-of-vaporization [$\Delta H_v(298)$], and enthalpies-of-sublimation [$\Delta H_s(298)$] of azide-functionalized compounds was evaluated. The models, which rely on B3LYP/6-31G(d) characterizations of the electronic properties of an isolated molecule of a compound, include (1) an atom-equivalent (AE) approach for estimating $\Delta_f H_g^0(298)$ and (2) correlations for estimating $\Delta H_v(298)$ and $\Delta H_s(298)$ from properties of the electrostatic potential on an electron isodensity surface. Based on the validation effort, the need to add an equivalent to the AE model that is tailored for azide groups was identified and addressed. However, the AE model's estimates are still prone to systematic error, and $\Delta_f H_g^0(298)$ estimates derived from B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) calculations are recommended. $\Delta H_v(298)$ estimates for azide-functionalized compounds proved to be in reasonable agreement with values derived from experiments and from molecular dynamics simulations. Direct validation of $\Delta H_s(298)$ estimates was not obtained, but $\Delta_f H_g^0(298)$ estimates derived from $\Delta_f H_g^0(298)$ and $\Delta H_s(298)$ estimates were found to be in reasonable agreement with $\Delta_f H_g^0(298)$ values derived from experiments. With the validity of the models for azide-functionalized compounds so established, "best estimates" were obtained for a set of compounds with multiple azide groups that was synthesized by the U.S. Army Armament Research, Development, and Engineering Center.</p>				
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1. Introduction

Seeking to develop lead-free (Pb-free) primary explosives, the US Army Armaments Research, Development, and Engineering Center (ARDEC) synthesized a series of compounds with multiple azide groups (Surapaneni et al., 2002; Dave et al., 2004). Shown in figures 1 and 2, these compounds also have potential as energetic plasticizers, and they could be exploited to prepare novel dendritic structures.

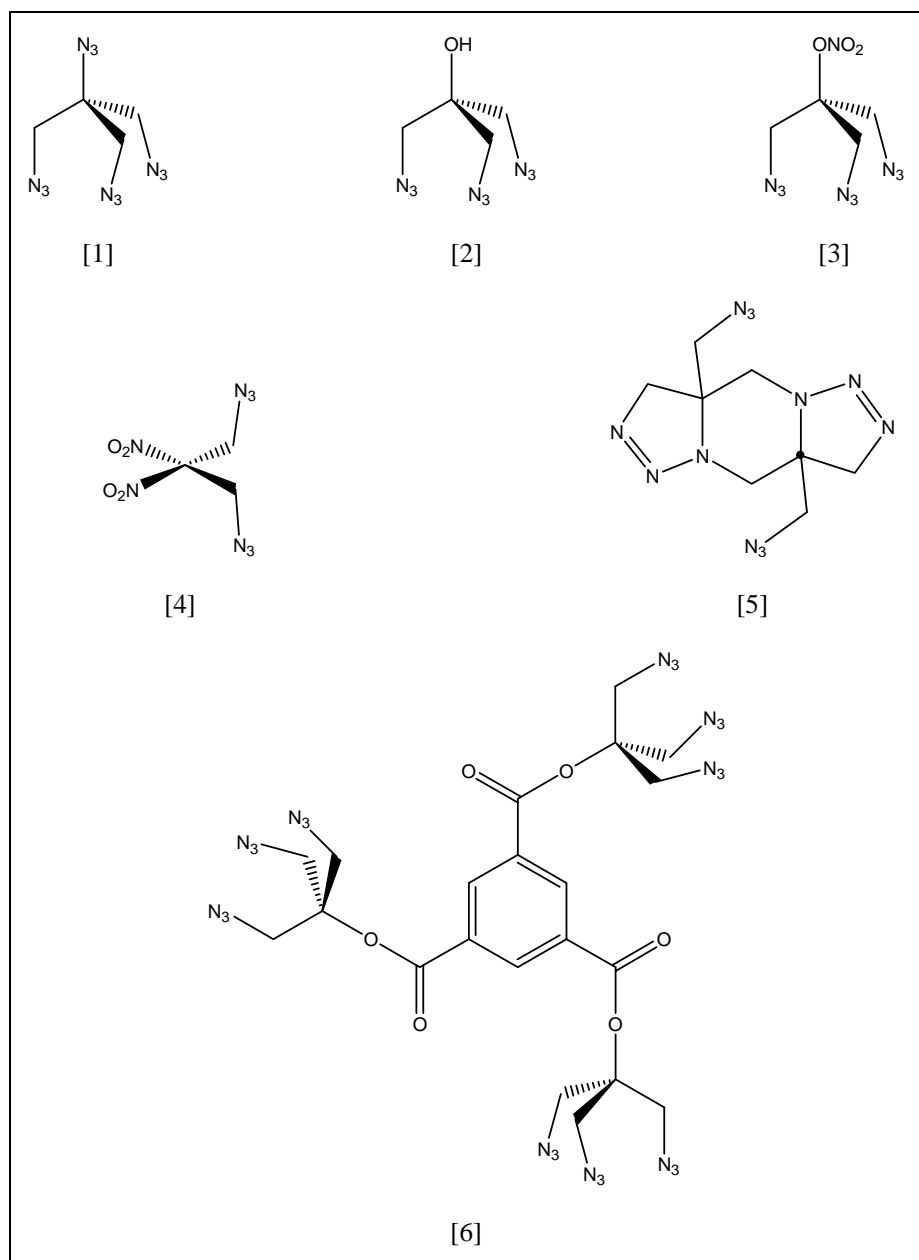


Figure 1. ARDEC-synthesized polyazido compounds: [1] – [6].

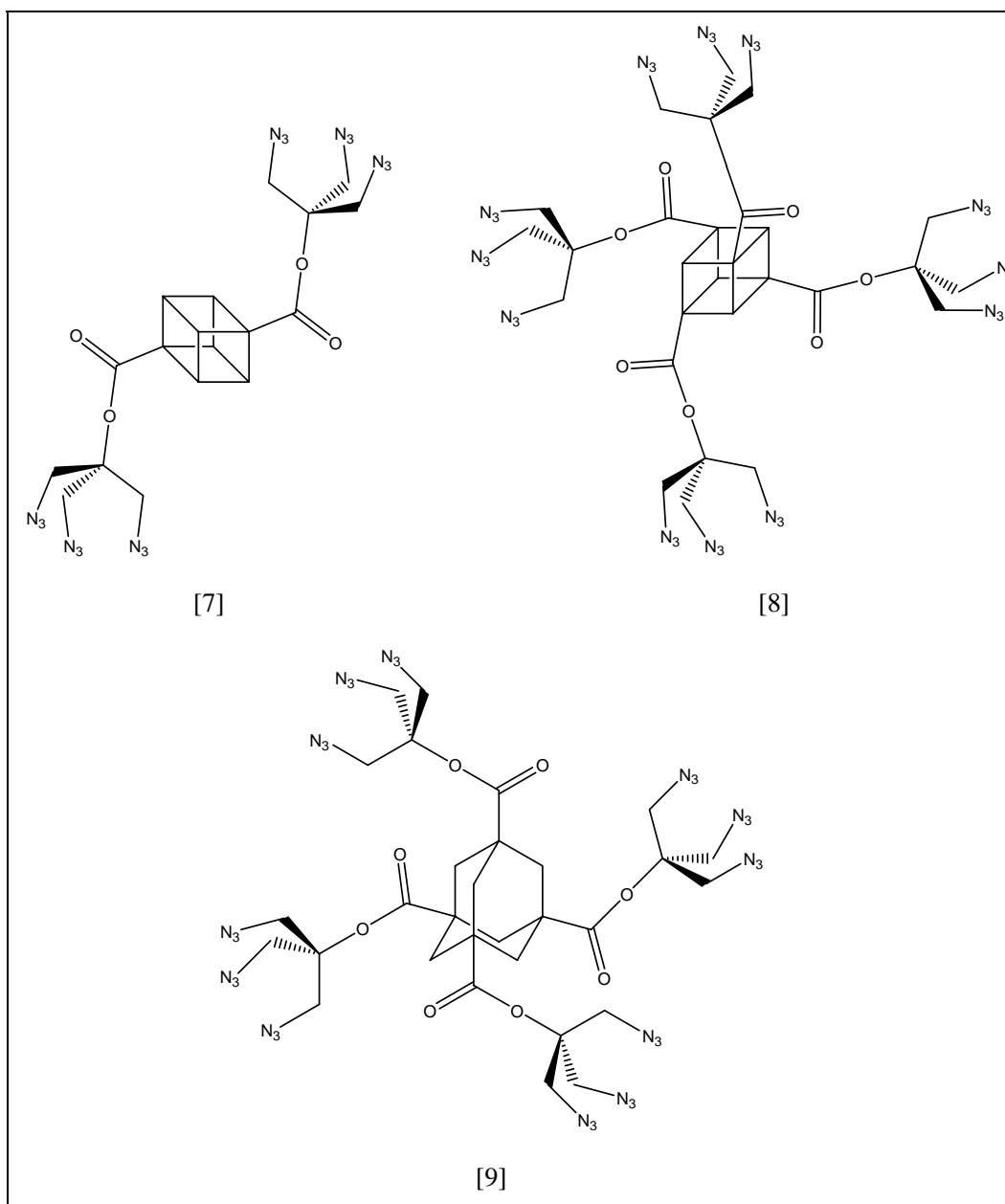


Figure 2. ARDEC-synthesized polyazido compounds: [7] – [9].

Desiring condensed-phase enthalpy-of-formation [$\Delta_f H_c^0(298)$] estimates for performance predictions and wanting to avoid “less than normally reliable” experimentally based determinations (Gray and Waddington, 1956), ARDEC asked the U.S. Army Research Laboratory to estimate them via semi-empirical models developed by Rice, Pai, and Hare (RPH) (Rice et al., 2000). Those models include (1) a density functional theory (DFT)-based “atom-equivalent” (AE) approach for estimating gas-phase enthalpies-of-formation [$\Delta_f H_g^0(298)$] and (2) correlations for estimating enthalpies-of-sublimation [$\Delta H_s(298)$] and enthalpies-of-vaporization [$\Delta H_v(298)$]. The attractiveness of the RPH models for the given application was

that they were parameterized for use in obtaining estimates for “energetic materials.” [That is, any compound whose molecules are functionalized with at least one $-\text{NO}_2$ (nitro-), $-\text{ONO}$ (nitrite), $-\text{ONO}_2$ (nitrate), $-\text{NNO}_2$ (nitramine), or $-\text{N}_3$ (azide) group.] Indeed, data for azide functionalized compounds were included in the training sets employed to parameterize the models. However, there were several concerns about the RPH models’ validity for the given application that needed to be addressed prior to providing the requested estimates. Those concerns and their resolution are discussed here.

2. Background

RPH discuss common approaches for converting quantum mechanically (QM)-determined atomic and/or molecular energies into $\Delta_f H_g^0(298)$ estimates (Rice et al., 2000). Methods based on high-level treatment of the electronic energy, e.g., the G2 method (Curtiss et al., 1991), are generally considered the most reliable. However, they become computationally intractable for “large” molecules. [In the case of G2, “large” is 7 or so “heavy” (i.e., nonhydrogen) atoms.] Thus, they cannot be employed for the molecules in figures 1 and 2. Instead, methods designed to address systematic biases that can be introduced by lower level treatments of electronic energy must be employed. AE models are one such approach (Wiberg, 1984).

The equation for an AE model may be written

$$\Delta_f H_g^0(i, 298) = E(i) - \sum_j n(j) \epsilon(j), \quad (1)$$

where $E(i)$ is the QM-determined electronic energy of the molecule of interest (i), $n(j)$ is the number of j -type atoms in the molecule, and $\epsilon(j)$ is the so-called “atom equivalent” of “atom-type” j . (Atom-types are definitions based on a heuristic description of an atom’s local bonding environment.) The $\epsilon(j)$ for a given model are determined by computing the $E(i)$ for a training set of molecules with “established” (i.e., experimentally derived) $\Delta_f H_g^0(298)$ values and performing a least squares fit of equation 1 to the data. [As will be discussed, the basis and reliability of “established” $\Delta_f H_g^0(298)$ values can widely vary.]

Because AE models are semi-empirical, one’s $\Delta_f H_g^0(298)$ estimate for a compound will be suspect unless all of the atoms in the compound have local bonding environments that are similar to those found in the model’s training set. [Note also that because $E(i)$ values are theory and basis set dependent, to obtain a reliable estimate for a given compound/molecule with a given model, the molecule’s $E(i)$ must be calculated with the same theory and basis set utilized in calculating the training set’s $E(i)$ data.] Needing estimates for energetic materials being developed for the formulation of propellants and explosives, and the molecules of such materials having relatively unique electronic/bonding properties, RPH parameterized an AE model based on a 35-compound set of C, H, N, and O containing compounds having at least one $-\text{NO}_2$, $-\text{ONO}$,

–ONO₂, –NNO₂, or –N₃ group. Calculating molecule $E(i)$ s via B3LYP/6-31G(d) calculations (Becke, 1993; Lee et al., 1988; Miehlich et al., 1989; Petersson and Al-Laham, 1991) and defining seven different atom types: (1) C, H, N, or O atoms connected to other atoms via single bonds only and (2) C, N, or O atoms connected to other atoms via one or more multiple bonds (and designated C', N', and O', respectively), the resulting (RPH AE) model yielded $\Delta_f H_g^0(298)$ estimates that, with respect to the training set data, had a root mean square (RMS) deviation of 3.1 kcal/mol and a maximum (single) deviation of 7.3 kcal/mol.

The models developed by RPH for estimating $\Delta H_v(298)$ and $\Delta H_s(298)$ follow from the work of Politzer and coworkers (Murray and Politzer, 1994; Politzer et al., 1997). Those researchers found that, for “a general class of organic molecules,” the $\Delta H_v(298)$ and $\Delta H_s(298)$ of a compound correlate with electrostatic potential properties of an electron isodensity surface for an isolated molecule of the compound. Their correlation for obtaining $\Delta H_v(298)$ estimates has the form

$$\Delta H_v(298) = a_v \sqrt{SA} + b_v \sqrt{\sigma_{tot}^2} v + c_v, \quad (2)$$

where SA is the area of the 0.001 electron/bohr³ surface of the molecule, σ_{tot}^2 is a measure of the variability of the electrostatic potential on this surface, and v is a measure of the “balance” between positive and negative charges on the surface. The constants a_v , b_v , and c_v are established by fitting equation 2 to $\Delta H_v(298)$, SA , σ_{tot}^2 , and v values for a training set of molecules. Like an AE model's $\mathcal{E}(j)$, a $\Delta H_v(298)$ estimation model's constants depend on the theory and basis set employed to compute the electronic properties of the training set molecules. RPH parameterized equation 2 based on (1) B3LYP/6-31(d)-calculated SA , σ_{tot}^2 , and v values and (2) experimentally derived $\Delta H_v(298)$ values for 27 energetically functionalized compounds. Their model produced estimates for the training set whose RMS deviation from the experimentally derived values was 1.7 kcal/mol; and only one estimate was more than 3 kcal/mol different from its corresponding experimental value.

Similarly, RPH parameterized a correlation between isolated molecule electrostatic potential properties and $\Delta H_s(298)$, the form of which Politzer and coworkers had developed and validated for a general class of organic molecules (Politzer et al., 1997). That is,

$$\Delta H_s(298) = a_s (SA)^2 + b_s \sqrt{\sigma_{tot}^2} v + c_s. \quad (3)$$

In this case, RPH determined parameters a_s , b_s , and c_s by fitting the equation to experimentally derived $\Delta H_s(298)$ values and B3LYP/6-31G(d)-calculated SA , σ_{tot}^2 , and v values for a 36-constituent training set of energetically functionalized compounds. The resulting model produced estimates for the training set whose RMS deviation from their experimentally derived values was 3.6 kcal/mol; and only one $\Delta H_s(298)$ estimate was more than 6 kcal/mol different than its corresponding experimentally derived value.

Because RPH parameterized their models using data for molecules with energetic functional groups, the models were expected to be reasonably good starting points for estimating the properties of the ARDEC-synthesized compounds. However, there were concerns about their validity for the application because the number of azide compounds whose property data was included in the training sets was very limited. A particular concern was the parameterization of RPH's AE model. Because their training set for the model was heavily weighted with data for $-\text{NO}_2$ functionalized molecules, the model in effect assumes that the (heuristic) local bonding environment associated with a nitrogen atom linked to another atom (or atoms) via a multiple bond (or bonds) is $=\text{N}=\text{N}$ or $-\text{N}=\text{N}$. Thus, the bonding environment pictured for an azido group with nitrogen atoms so defined would be $-\text{N}=\text{N}=\text{N}-$. Since this bonding scheme would correspond to a state with lower electronic energy than the $-\text{N}=\text{N}\equiv\text{N}$ scheme typically understood to represent bonding in an azido group, it seemed likely that the RPH AE model would yield $\Delta_f H_g^0(298)$ estimates for azides that were too negative. Moreover, since the expected bias would be multiplied by the number of azide functional groups in the molecule of interest, it was considered necessary to validate its use for estimating the $\Delta_f H_g^0(298)$ values of the ARDEC-synthesized compounds.

Being based on computed properties of the electron cloud surrounding a molecule rather than crudely defined local bonding environments for individual atoms, the RPH $\Delta H_v(298)$ and $\Delta H_s(298)$ estimation models are considered more general in nature than the RPH AE model. Moreover, they are void of parameters that, like the $\alpha(j)$ of RPH AE model, have the potential to produce additive errors. Therefore, a mismatch between the atom types of the compound of interest and those of the molecules whose data are employed to parameterize the correlations is considered less likely to produce significant systematic error. Nevertheless, confirmation that RPH's $\Delta H_v(298)$ and $\Delta H_s(298)$ estimation models would yield reasonable estimates for azides was sought.

To validate the RPH models' estimates for azide-functionalized compounds, a literature search for experimentally derived azide $\Delta_f H_g^0(298)$, $\Delta H_v(298)$, and $\Delta H_s(298)$ data was conducted. The search yielded a 16-compound set of $\Delta_f H_g^0(298)$ values, an 8-compound set of $\Delta_f H_s^0(298)$ values, a 16-compound set of liquid-phase enthalpy-of-formation [$\Delta_f H_l^0(298)$] values, and a 16-compound set of $\Delta H_v(298)$ values. No experimentally derived $\Delta H_s(298)$ data were found. Considered minimal (at best) for the intended validation effort, the data's shortcomings due to scarcity are exacerbated by the fact that the reliability of much of it can be questioned. Some were considered "preliminary" (Murrin and Carpenter, 1957) or "approximate" (Lee et al., 1989) by the authors who published it. Some were not subject to peer review (Thompson, 2000); or if found in a peer-reviewed paper, the context suggests that it would have been difficult for a reviewer to judge its merit (Wayne et al., 1993). And even data that appear to meet high standards (Fagley and Myers, 1954; Fagley et al., 1953) have been questioned by others (Evans et al., 1959; Pepkin et al., 1993).

Because the quantity of “unquestionably reliable,” experimentally derived thermochemical property data for azides is scant, $\Delta_f H_g^0(298)$ and $\Delta H_v(298)$ estimates based on alternate computational methodologies were also obtained. For a set of molecules with seven or fewer heavy atoms, alternate $\Delta_f H_g^0(298)$ estimates were obtained via two different G2-based methods. One is based on atomization enthalpies and will be referred to as the “G2-ae” method. The other is based on enthalpies-of-reaction [$\Delta_r H^0(298)$] for “isodesmic reactions” and will be referred to as the “G2-ir” method. [Isodesmic reactions are reactions in which the total number of each bond type is equal in reactants and products (Foresman and Frisch, 1996).] In addition, for most compounds with a $\Delta_f H_g^0(298)$ value derived via any other manner, a $\Delta_f H_g^0(298)$ estimate was derived from B3LYP/6-311++G(d,p)//B3LYP/6-31G(d)-determined $\Delta_r H^0(298)$ for an isodesmic reaction. This method will be referred to hereafter as the “DFT” method. Alternate $\Delta H_v(298)$ estimates were obtained from molecular dynamics (MD) simulations, some of which have been previously reported (McQuaid et al., 2004).

The alternate $\Delta_f H_g^0(298)$ estimation methods employed to validate the RPH AE model deserve comment. The DFT method, i.e., the conversion of $\Delta_r H^0(298)$ into $\Delta_f H_g^0(298)$ of a reaction component i , is based on Hess’s Law,

$$\begin{aligned}\Delta_r H^0(298) &= \sum_p n(p)H(p, 298) - \sum_r n(r)H(r, 298) \\ &= \sum_p n(p)\Delta_f H_g^0(p, 298) - \sum_r n(r)\Delta_f H_g^0(r, 298).\end{aligned}\quad (4)$$

By rearranging this equation,

$$\begin{aligned}\Delta_f H_g^0(i, 298) &= \left(\sum_p n(p)H(p, 298) - \sum_r n(r)H(r, 298) \right) \\ &\quad - \left(\sum_{p \neq i} n(p)\Delta_f H_g^0(p, 298) - \sum_r n(r)\Delta_f H_g^0(r, 298) \right),\end{aligned}\quad (5)$$

it is observed that $\Delta_f H_g^0(i, 298)$, which for this discussion we assume is a product (p), can be determined from the computed enthalpies of products [$H(p, 298)$] and reactants [$H(r, 298)$] if the $\Delta_f H_g^0(298)$ of all remaining reactants and products are known. Though such calculations can, in principle, be based on any stoichiometrically correct reaction, estimates based on isodesmic reactions are thought to have better accuracy than estimates derived from other reaction schemes because systematic errors in the calculation of electronic energies cancel (Foresman and Frisch, 1996).

With a significant portion of the necessary computational effort already completed in obtaining $E(i)$ values for the RPH AE model, the DFT method provides a relatively simple check of the more empirical method. The DFT method can be constructed to rely on a different—and perhaps more reliable—experimentally derived $\Delta_f H^0(298)$ database. [The unique electronic

structure/bonding in the azido group dictates that at least one, hopefully highly reliable, $\Delta_f H_g^0(R - N_3, 298)$ value be utilized, but the same one (or ones) need not be in the RPH AE model training set.] Also, it does not utilize empirical parameters to account for systematic errors in the calculation of $E(i)$ or the thermal energy contributions to the enthalpy [$\Delta H(i) = H(i, 298) - H(i, 0)$]. [$\Delta H(i)$ accounts for the enthalpic contributions of higher energy electronic states and vibrational, rotational, and translational motion.] Moreover, the approach has the potential to mitigate errors introduced by the inadvertent use of strained (i.e., relatively high energy) reference structures. The primary shortcoming of the DFT method as a check of the RPH AE model is that it employs the same (B3LYP) theoretical basis. Though B3LYP-based calculations have been shown to reproduce the structure and normal modes of azide-functionalized compounds (Costa Cabral and Costa, 1995; McQuaid et al., 2002), its appropriateness for determining azide $\Delta_f H_g^0(298)$ values has not, to our knowledge, been rigorously examined.

Lacking such validation, and concerned that a bias in B3LYP-based determinations might not be revealed by a comparison of RPH AE model and DFT method results alone, comparisons with estimates from ab initio-based methods were sought, with the G2-ir and G2-ae methods ultimately being chosen for this purpose. (G2-based calculations employ ab initio theories to optimize geometries and compute energies.) The G2-ir method was utilized to recalculate the $\Delta_f H^0(298)$ values for the isodesmic reactions constructed for the DFT method. Since the $\Delta_f H^0(298)$ predictions for the two methods rely on the same $\Delta_f H^0(298)$ database, differences have the potential to be attributable to a failure of one of the theoretical bases.

The G2-ae method is probably the most common approach for converting G2-based calculations into $\Delta_f H^0(i, 298)$ estimates. Based on a variation of equation 5, viz.,

$$\Delta_f H_g^0(i, 298) = H(i, 298) - \sum_r n(r)H(r, 298) + \sum_r n(r)\Delta_f H_g^0(r, 298), \quad (6)$$

it employs a set of $\Delta_f H_g^0(r, 298)$ values that is completely different from the one employed by the DFT and G2-ir methods, i.e., those for C, H, N, and O atoms. An estimate from this method still depends on whether a representative conformer for the molecule of interest is employed for the calculation of $H(i, 298)$, but a comparison of G2-ae method estimates with G2-ir method estimates has the potential to expose anomalies in the $\Delta_f H_g^0(298)$ data utilized for the G2-ir and DFT methods.

The validation effort indicated that the RPH AE model yielded $\Delta_f H_g^0(298)$ estimates for azides that were indeed too negative. However, the set of experimentally derived $\Delta_f H_g^0(298)$ values employed in the validation effort was considered too small and questionable a basis for the parameterization effort required to address the situation. Moreover, no experimentally derived $\Delta H_s(298)$ data for azides were found, so it was not possible to directly validate the RPH $\Delta H_s(298)$ estimation model. Therefore, it was considered that a parameterization based on data that included $\Delta_f H_g^0(298)$ values derived from (1) experimentally determined liquid-phase

enthalpies-of-formation [$\Delta_f H_l^0(298)$] or $\Delta_f H_s^0(298)$ values and (2) RPH $\Delta H_v(298)$ or $\Delta H_s(298)$ estimates would be preferable. Not only would the size of the $\Delta_f H_g^0(298)$ training set increase, by coupling the experimentally derived $\Delta_f H^0(298)$ values and RPH enthalpy-of-phase-change estimates, the approach was considered to have the potential to mitigate systematic errors in the latter if they existed.

Beyond the need to evaluate the validity of the RPH models for estimating the thermochemical properties of azides, there were difficulties in employing the models for some of the molecules in figures 1 and 2. For one, even with the relatively modest [B3LYP/6-31G(d)] theoretical basis underlying the models, obtaining optimization solutions that meet typical convergence criteria is still a challenge for molecules as large as [8] and [9]. Moreover, they have thousands of equilibrium conformations, and it is not possible to know from simple inspection whether the energies of structures obtained from arbitrary starting points are representative of the values for structures that will exist in a room temperature sample of the compound. In principle, one could systematically search a molecule’s conformational space based on presumed dihedral angle preferences, but the resources needed to perform such a search via QM methods are not practical. To address this issue, a quenched MD routine was developed and employed to search for low energy structures.

3. Computational Methods

3.1 Quantum Chemistry Calculations

Gaussian 03 (G03) (Frisch et al., 2003) was employed to perform all of the quantum chemistry calculations. Included were (1) B3LYP/6-31G(d) optimizations, (2) B3LYP/6-31G(d) normal mode calculations, (3) B3LYP/6-311++G(d,p) (Krishnan et al., 1980; Frisch et al., 1984; Clark et al., 1983) single point energy calculations for the B3LYP/6-31G(d) optimized structures, and (4) G2 calculations of molecule and atom enthalpies. The starting structures for the optimizations of all compounds except those in figures 1 and 2 were generally chosen based on our best guess for a low energy structure, but consistency, particularly between the reactants and products of an isodesmic reaction scheme, was also a consideration. For example, alkyl chains with more than three carbon atoms were always constructed to be linear. And for primary azide groups ($-\text{CH}_2\text{-N}_3$), *anti* conformers ($-\text{C-C-N-N-}$ dihedral angle equal 180°) rather than *gauche* conformers ($-\text{C-C-N-N-}$ dihedral angle equal $\sim 65^\circ$) were built. The convergence criteria for the optimizations were maximum force ≤ 0.000450 hartree/bohr, RMS force ≤ 0.000300 hartree/bohr, maximum displacement ≤ 0.001800 bohr, and RMS displacement ≤ 0.001200 bohr. Normal mode calculations were performed for molecular structures meeting the optimization convergence criteria to confirm that they were indeed equilibrium configurations.

The G2 calculations were performed as prescribed by G03. Starting structures for the calculations were obtained from B3LYP/6-31G(d) optimizations. G03's protocol for the G2 calculation first obtains a HF/6-31(d) optimized geometry from the starting structure, then performs a frequency calculation to estimate the structure's zero-point vibrational energy (ZPVE). The HF/6-31G(d) optimized structure is then reoptimized using MP2(Full)/6-31G(d), and the resulting structure is employed for all subsequent calculations. Those calculations include computing a base electronic energy using MP4/6-311G(d,p) and making corrections to it based on MP4/6-311+G(d,p)-, MP4/6-311G(2df,p)-, and QCISD(T)/6-311G(d,p)-calculated single point energies. The method also dictates that the base energy be corrected for the "residual" correlation energy between spin-paired electrons. This correction is estimated with an empirically-based formula.

For large molecules, it is usual that numerous different isodesmic reactions can be postulated to obtain $\Delta_f H_g^0(298)$ estimates. However, we focused on and were successful in finding ones in which the molecule of interest and $n\text{H}_2$ ($n \geq 1$) were the only products. G03 calculations of reactant, product, and reference molecule $H(298)$ values were employed (unscaled) in the derivation of the $\Delta_f H_g^0(298)$.

G03 was also employed to generate molecule 0.001 electron/bohr³ surfaces and map the electrostatic potential on these surfaces. All of the G03-generated data that were used in estimating the thermochemical properties reported in this report are included in the appendix. Experimentally derived thermochemical data and their source are also included there.

3.2 Molecular Dynamics Calculations

3.2.1 Enthalpy-of-Vaporization Estimates

In addition to RPH $\Delta H_v(298)$ estimates, $\Delta H_v(298)$ estimates were obtained from MD simulations. The simulations were performed with the Discover program (Accelrys, Inc., 2002) and the COMPASS force field (Sun, 1998; McQuaid et al., 2004). The COMPASS force field was chosen because, with azide atom types having recently been added (McQuaid et al., 2004), it includes parameters appropriate for all of the atom types found in the molecules of interest. Cubic, three-dimensional, periodic cells with ~1250 atoms (56–72 molecules) were constructed with the AmorphousCell module of InsightII. From three to five different cells were built for each compound, with all of them having an initial target density of 0.9 g/cm³. The cube edge lengths for the cells produced by this procedure were ~25 Å. The dynamics were modeled with Verlet velocity integration (Swope et al., 1982) and Andersen temperature control (Andrea et al., 1983). Berendsen pressure control (Berendson et al., 1984) was employed to model constant pressure and temperature (NPT) dynamics. A group-based cut-off method with tail correction was employed to evaluate nonbond interactions. The cut-off method assumes that the radial distribution functions converge to unity beyond the cut-off distance. The cut-off distance was specified to be 10 Å for all simulations.

The simulations consisted of three stages. The first stage was a 30,000 step, 1-fs/step, constant volume and temperature “pre-equilibration” simulation run to relieve large stresses inadvertently introduced by the cell packing procedure. The second stage was a 30,000 step, 1-fs/step NPT simulation that allowed the cell to equilibrate. The final stage was a 50,000 step, 1-fs/step NPT simulation during which the “cohesive energy density” (E_{CED}) was calculated. E_{CED} , which is defined as the average intermolecular nonbond energy per unit volume, is related to $\Delta H_v(298)$ per

$$\Delta H_v(298) = E_{CED}M / \rho + 298 * R, \quad (7)$$

where M is the molecular weight, ρ is the density, and R is the universal gas constant.

3.2.2 Conformer Searches

A quenched MD routine was implemented to search for low energy conformers of the ARDEC-synthesized compounds. Like the MD simulations performed to obtain $\Delta H_v(298)$ estimates, the routine was performed with the Discover program and the COMPASS force field. The routine involved sequentially heating, optimizing to a (local) minimum, then recording the structure and energy of an isolated molecule over hundreds to thousands of cycles. The magnitude and duration of the heating phase were established on a case-by-case basis through trial-and-error, the goal of each search being to find conditions such that the molecule occasionally accessed structures with energies 5–10 kcal/mol higher than the lowest-energy structure established to that point. The procedure was tested for the case of 2-azido-N,N-dimethylethanamine (DMAZ). Based on presumed dihedral angle preferences, this molecule has 14 possible equilibrium conformations, and they had been systematically searched for in a previous study via B3LYP/6-311++G(d,p) calculations (McQuaid et al., 2002). In that study, 12 of the 14 possibilities were observed and steric interference was shown to preclude the remaining two. The quenched MD routine quickly identified the 12 established conformers, and it did not produce any “artificial” ones. Moreover, the relative energies of the conformers calculated by the molecular model were in reasonable agreement with the B3LYP/6-311++G(d,p) results.

4. Results and Discussion

4.1 Initial Validation of the RPH Models

4.1.1 Gas-Phase Enthalpies-of-Formation

Table 1 compares experimentally derived $\Delta_f H_g^0(298)$ values with estimates based on the RPH AE model and the DFT method. In 13 of the 16 cases, the estimate obtained via the RPH AE model is less than the experimentally derived value. And for the three compounds where the RPH AE model estimate is higher than the experimentally derived value—azidocyclopentane, azidocyclohexane, and cyanogen azide—the reliability of the experimentally derived values is

Table 1. Comparison of experimentally derived and estimated $\Delta_f H_g^0(298)$ values (kcal/mol).

Compound	Exp	RPH AE ^a	DFT	Isodesmic Reaction
Hydrogen azide	71.7 ^b	67.4	—	—
1-Azidopentane	46.1 ^c	41.5	52.7	Pentane+HN ₃ → 1-Azidopentane + H ₂
1-Azidohexane	47.4 ^c	36.5	47.7	Hexane+HN ₃ → 1-Azidohexane + H ₂
1-Azidoheptane	41.1 ^c	31.5	42.8	Heptane+HN ₃ → 1-Azidoheptane + H ₂
1-Azidooctane	35.9 ^c	26.4	37.9	Octane+HN ₃ → 1-Azidooctane+H ₂
3-Azido-3-ethylpentane	40.6 ^d	31.8	39.7	3-Ethylpentane+HN ₃ → 3-Azido-3-ethylpentane+H ₂
1-Azidoadamantane	51.6 ^d	51.2	50.8	Adamantane+ HN ₃ → 1-Azido-adamantane+H ₂
2-Azido-N,N-dimethyl-ethanamine	76.2 ^e	68.5	79.9	Dimethylamine+Ethane+ HN ₃ → 2-Azido-N,N-dimethylethanamine+2H ₂
Azidotritromethane	84.2 ^f	80.3	90.2	Trinitromethane+HN ₃ → Trinitroazidomethane+H ₂
1-Azido-1,1-dinitroethane	60.4 ^f	54.3	63.4	1,1-Dinitroethane+ HN ₃ → 1-Azido-1,1-dinitroethane+H ₂
Azidobenzene	93.0 ^g	92.8	102.8	Benzene+HN ₃ → Azidobenzene+H ₂
Azidomethylbenzene	99.5 ^f	93.0	102.0	Methylbenzene+HN ₃ → Azidomethylbenzene+H ₂
2-Azido-2-phenylpropane	87.4 ^d	73.5	86.4	2-Phenylpropane+HN ₃ → 2-Azido-2-phenylpropane+H ₂
Azidocyclopentane	52.8 ^h	58.4	67.0	Cyclopentane+HN ₃ → Azidocyclopentane+H ₂
Azidocyclohexane	36.9 ^h	47.0	56.2	Cyclohexane+HN ₃ → Azidocyclohexane+H ₂
Cyanogen azide	108.0 ⁱ	114.2	122.7	HCN+HN ₃ → NCN ₃ +H ₂

^aBased on the parameters in Rice et al. (2000).

^b(Gray and Waddington, 1956).

^cCalculated based on condensed-phase enthalpy-of-formation values in Murrin and Carpenter (1957) and enthalpy-of-vaporization values in Lee et al. (1989).

^d(Wayne et al., 1993).

^e(Dee, 2000).

^f(Pepkin et al., 1993).

^gCalculated from the condensed-phase enthalpy-of-vaporization value in Pepkin et al. (1993) and a condensed phase enthalpy-of-formation value. Pepkin et al. attributes to Roth and Mueller (1929).

^h(Fagley and Myers, 1954).

ⁱ(Okabe and Mele, 1969).

doubtful. The experimentally derived $\Delta_f H_g^0(298)$ values for azidocyclopentane and azidocyclohexane have long been questioned (Gray and Waddington, 1956), and, as will be discussed, other theoretical results support a higher $\Delta_f H_g^0(298)$ value for cyanogen azide.

Figure 3 shows the differences between experimentally derived $\Delta_f H_g^0(298)$ values and the RPH AE model estimates for the 13 cases in which the experimental data are considered reliable. Anticipating results yet to be presented, differences are plotted as a function of the number of atoms in the molecule. The average difference between the RPH AE model estimates and the experimentally derived values is 6.1 kcal/mol. On this basis, the addition of an azide-group equivalent [$\alpha(\text{N}_3)$] to the model was judged to be necessary.

Figure 3 also plots the differences observed between experimentally derived $\Delta_f H_g^0(298)$ values and their corresponding DFT estimates. In general, the DFT estimates are higher than the experimentally derived values, with the average difference for the 12 cases compared being 2.6 kcal/mol. Considered an indication of systematic error, we focused on two potential sources of it: (1) a bias due to B3LYP and (2) the systematic manner in which the isodesmic reaction

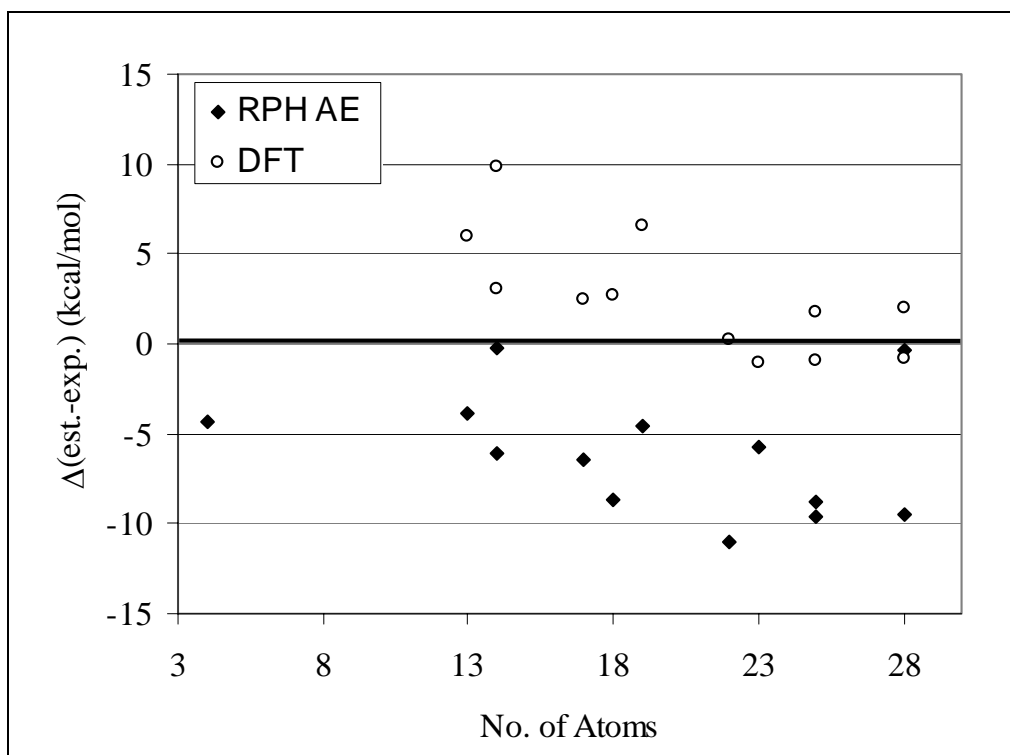


Figure 3. Differences between estimated and experimentally derived $\Delta_f H_g^0(298)$ values.

schemes were constructed. With respect to the latter possibility, there were two considerations. The first was that all of the isodesmic reactions employ HN_3 as a reactant. Therefore, any error in the $\Delta_f H_g^0(298)$ value that we used for the calculations is added to the estimate of every compound. Our second concern was that in all of the (hypothetical) reaction schemes we constructed, only heavy-atom—H bonds are broken and only H—H and heavy-atom—heavy-atom (single) bonds are formed. Therefore, any systematic bias in the calculation of the electronic energy that corresponds to these bond types will propagate into the $\Delta_f H_g^0(298)$ estimates.

The DFT, G2-ae, and G2-ir estimates presented in table 2 were analyzed in an attempt to address the issues raised. The G2-ae estimates for hydrogen azide, azidomethane, and (*anti*-)azidoethane reproduce those of Rogers and McLafferty (RM) (1995). Small differences between their results and those in table 2 are due to the use of different methods for calculating $\Delta H(i)$. The G2-ae $\Delta_f H_g^0(298)$ estimate for HN_3 is 1.4 kcal/mol lower than the value Gray and Waddington (GW) (1956) derive from experimental data. (The reliability of the GW value is to be discussed.) RM do not compare their estimates to experimental values directly. However, finding that the $\Delta_f H_g^0(298)$ estimates for azidomethane and azidoethane are more negative than would be predicted on the basis of experimentally derived results for “higher homologous azides” (1-azidoadamantane, 3-azido-3-ethylpentane and 2-azido-2-phenylpropane) (Wayne et al., 1993), they hypothesize that the G2-ae estimates might be too negative.

Table 2. Comparison of RPH AE, G2-ae, G2-ir, and DFT $\Delta_f H_g^0(298)$ estimates (kcal/mol).

Compound	RPH AE ^a	G2-ae	G2-ir	DFT	Isodesmic Reaction
Hydrogen azide	67.4	70.3 ^b	—	—	—
Cyanogen azide	114.2	120.7	122.5	122.7	$\text{HCN} + \text{HN}_3 \rightarrow \text{NCN}_3 + \text{H}_2$
Azidomethane	64.1	72.3 ^b	72.2	73.8	$\text{Methane} + \text{HN}_3 \rightarrow \text{Azidomethane} + \text{H}_2$
<i>gauche</i> -Azidoethane	56.7	66.1	64.8	67.5	$\text{Ethane} + \text{HN}_3 \rightarrow \text{Azidoethane} + \text{H}_2$
<i>anti</i> -Azidoethane	57.8	66.3 ^b	64.9	67.6	$\text{Ethane} + \text{HN}_3 \rightarrow \text{Azidoethane} + \text{H}_2$
1-Azidopropane	51.6	62.4	60.0	62.8	$\text{Propane} + \text{HN}_3 \rightarrow \text{1-Azidopropane} + \text{H}_2$
2-Azidopropane	49.4	58.5	56.0	60.3	$\text{Propane} + \text{HN}_3 \rightarrow \text{2-Azidopropane} + \text{H}_2$
1-Azidobutane	46.6	58.5	54.9	57.8	$\text{Butane} + \text{HN}_3 \rightarrow \text{1-Azidobutane} + \text{H}_2$
1-Azido-2-methylpropane	46.3	56.3	52.8	56.1	$\text{2-Methylpropane} + \text{HN}_3 \rightarrow \text{1-Azido-2-methylpropane} + \text{H}_2$
2-Azido-2-methylpropane	43.0	49.9	46.3	52.3	$\text{2-Methylpropane} + \text{HN}_3 \rightarrow \text{2-Azido-2-methylpropane} + \text{H}_2$
2-Azidoethanol	31.6	31.2	30.3	33.0	$\text{Ethanol} + \text{HN}_3 \rightarrow \text{2-Azidoethanol} + \text{H}_2$
1-Azido-3-ethylpentane	35.5	—	—	43.6	$\text{3-Ethylpentane} + \text{HN}_3 \rightarrow \text{1-Azido-3-ethylpentane} + \text{H}_2$
3-Azido-3-ethylpentane	31.8	—	—	39.7	$\text{3-Ethylpentane} + \text{HN}_3 \rightarrow \text{3-Azido-3-ethylpentane} + \text{H}_2$

^a Based on the parameters in Rice et al. (2000).

^b See also Rogers and McLafferty (1995).

As evidence to support their hypothesis, RM note that the azide group is different from most of the molecules employed to develop the G2 method and that the G2-calculated enthalpy of atomization of CO_2 , which has the same number of electrons as HN_3 , is too negative by 2.7 kcal/mol. This results in a $\Delta_f H_g^0(298)$ estimate for CO_2 that is too negative by the same value. But we do not consider this argument compelling; our estimates for 1-azido-2-methylpropane and 2-azido-2-methylpropane indicate that $\Delta_f H_g^0(298)$ estimates for primary azides will indeed be negatively biased if calculated on the basis of values for tertiary azides. We therefore sought direct comparisons for other azides that might corroborate the RM hypothesis. Unfortunately, the only azido compound other than hydrogen azide for which an experimentally derived $\Delta_f H_g^0(298)$ datum was available and a G2-ae estimate could be calculated (with reasonable resources) was cyanogen azide. In its case, the G2-ae estimate, like the DFT estimate, is approximately 14 kcal/mol more positive than the experimentally derived value. Thus, we consider the experimentally derived value to be unreliable.

Lacking experimentally derived data that could be used to corroborate or refute the possibility of the G2-ae estimates for azides being negatively biased, the issue was considered by comparing G2-ae estimates to estimates obtained via other methods. Figure 4 plots the differences between the G2-ae, G2-ir, and DFT estimates as a function of the number of atoms in the molecule. Comparing G2-ir and DFT estimates, where estimates for a given compound are based on the same isodesmic reaction and experimentally derived $\Delta_f H_g^0(298)$ data, it is observed that the DFT estimates are always more positive than the corresponding G2-ir estimates—the differences varying from 0.2 kcal/mol for cyanogen azide to 6.0 kcal/mol for 2-azido-2-methylpropane. Moreover, the differences tend to increase with the number of atoms in the molecule. Thus, a theory related bias is indicated.

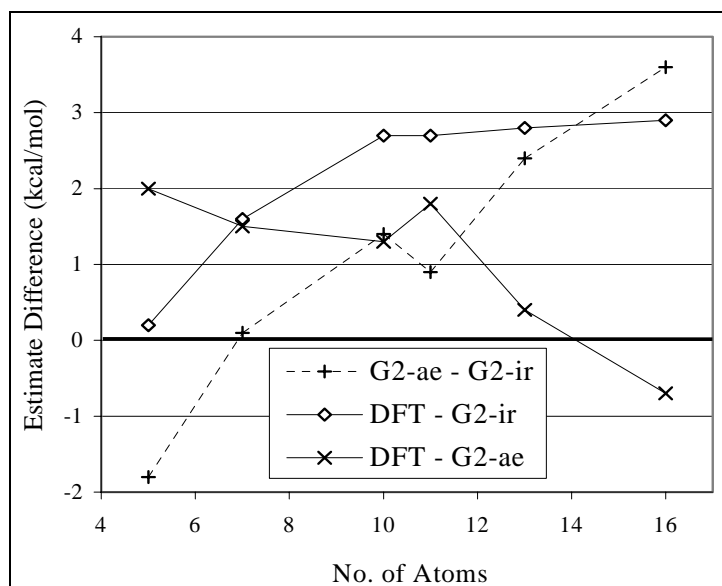


Figure 4. Differences between G2-ae, G2-ir, and DFT estimates.

Seeking the source of the bias, initial consideration was given to the methods' differences in calculating ZPVEs. In the G2-ir method they are computed based on HF/6-31G(d) calculations, while in the DFT method they are computed based on B3LYP/6-31G(d) calculations. Since the ZPVE scaling factors recommended for these two calculation types are significantly different, the ZPVE values from the two methods were compared. Table 3 shows the differences observed. They range between 0.25 and 0.31 kcal/mol for all but two molecules, and there is no size dependence. Thus, we conclude that the size-dependent trend in the difference between the G2-ir and DFT estimates is not due to differences in the methods' ZPVE calculations.

Table 3. Comparison of ZPVEs calculated with B3LYP/6-31G(d) and HF/6-31G(d).

Molecule	No. of Atoms	$\Delta(ZPVE)^a$
NC-N ₃	5	1.06
Azidomethane	6	-0.28
<i>anti</i> -Azidoethane	9	-0.31
<i>gauche</i> -Azidoethane	9	-0.28
1-Azidopropane	12	-0.28
2-Azidopropane	12	-0.29
1-Azidobutane	15	-0.25
1-Azido-2-methylpropane	15	0.24
2-Azido-2-methylpropane	15	-0.89
2-Azidoethanol	15	-0.31

^a $ZPVE[B3LYP/6-31G(d)] - ZPVE[HF/6-31G(d)]$.

The observation from figure 3 that the DFT $\Delta_f H_g^0(298)$ estimates, though too positive, tend to converge towards experimentally derived values as the number of atoms in a molecule increases, coupled with the observation from figure 4 that the G2-ir estimates diverge from the DFT estimates as the number of atoms in a molecule increases, suggests that the failure lies with the G2-ir method. This suspicion is supported by trends observed in $\Delta_f H_g^0(298)$ estimates for alkyl azides when plotted as a function of the number of methylene groups (see figure 5). That is, the G2-ae and DFT method estimates are in good agreement with each other and they extrapolate to the experimentally determined $\Delta_f H_g^0(298)$ values for longer chain molecules better than the G2-ir estimates. Based on this clue, $\Delta_f H_g^0(298)$ estimates for all linear alkanes with 7 or fewer carbon atoms were calculated via the G2-ae method. As shown in figure 6, the G2-ae estimates tend to diverge from the experimentally determined values as the number of methylene groups increases. The nature of the failure is uncertain; however, it appears that the G2-calculated $H(298)$ of the linear alkanes are too positive, and this bias manifests itself in the G2-ir calculations. (Presumably, the failure is mitigated by the addition of the azido group to the chain.)

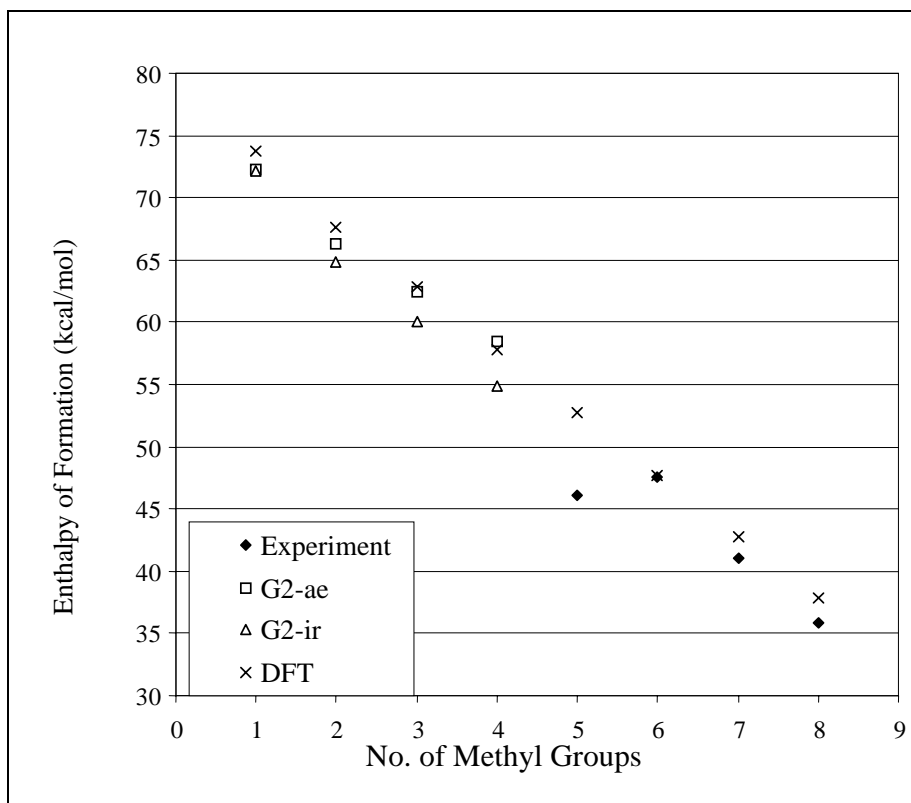


Figure 5. Estimated and experimentally derived $\Delta_f H_g^0(298)$ values for α -azidoalkanes.

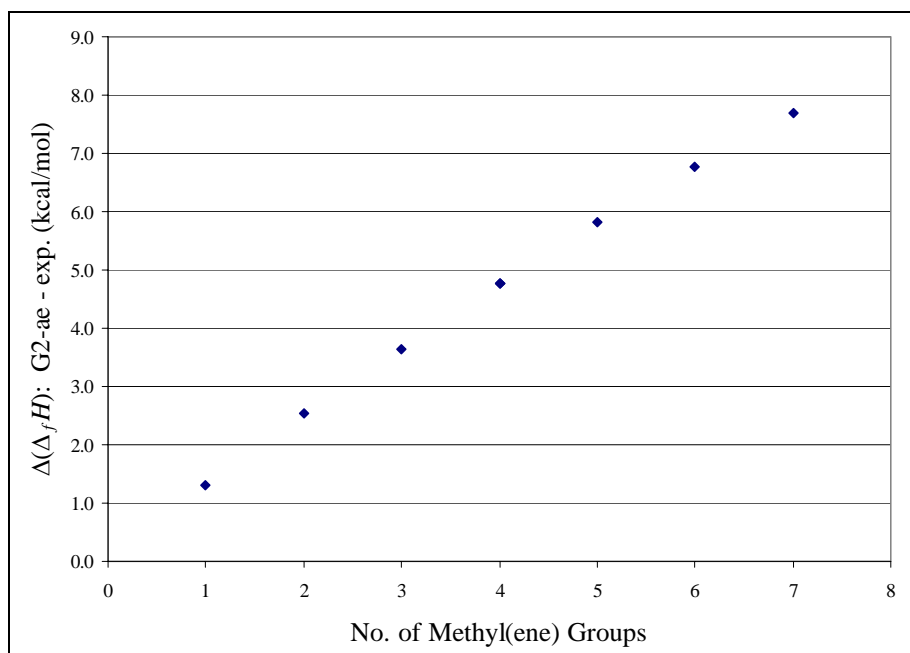


Figure 6. Difference between G2-ae and experimentally derived $\Delta_f H_g^0(298)$ values for linear alkanes.

The differences between the G2-ae and DFT estimates are not as significant as the differences between the G2-ir and DFT estimates. For the 10 compounds for which both G2-ae and DFT estimates were obtained, the average of the DFT estimates is 1.2 kcal/mol higher than the average of the G2-ae estimates. Since the average of the DFT estimates is 2.6 kcal/mol higher than experimentally derived values, and the differences tend to be larger for smaller molecules, the comparisons do not support the RM's hypothesis that the G2-ae estimates for azides are systematically low.

Our concern about systematic bias arising from the use of HN_3 as a reactant in all of the isodesmic reaction schemes employed to derive $\Delta_f H_g^0(i, 298)$ from equation 5 is primarily due to the $\Delta_f H_g^0(\text{HN}_3, 298)$ value we have employed for that purpose. That value (71.66 kcal/mol) is based on the recommendation of Gray and Waddington (GW) (1956; Evans et al., 1959), who derived it from (1) their measurements of the enthalpy-of-formation and enthalpy-of-neutralization of the aqueous azide ion and (2) the enthalpy-of-solution and $\Delta H_v(\text{HN}_3, 298)$ measured by Gunther, Mayer, and Muller-Skjold (GMM) (1935). The GW value is 1.4 kcal/mol higher than the nominal value GMM derived by coupling their $\Delta H_v(298)$ measurement with a $\Delta_f H_l^0(298)$ value derived from heat-of-combustion experiments. If the nominal GMM $\Delta_f H_g^0(298)$ value (70.3 kcal/mol) is employed for the DFT calculations in lieu of the GW value, the mean difference between the nine corresponding DFT and G2-ae estimates reduces to 0.0 kcal/mol and the mean difference between the 12 (seemingly reliable) experimentally derived $\Delta_f H_g^0(298)$ values and the corresponding DFT estimates reduces to 1.2 kcal/mol. Though such results suggest that $\Delta_f H_g^0(\text{HN}_3, 298)$ may be closer to 70.3 kcal/mol than to 71.66 kcal/mol, Gray and

coworkers state that their recommendation “may be expected to be correct to ± 0.2 kcal/mol” (Evans et al., 1959). While it is hard to imagine that error limits less than ± 1 kcal/mol are justified, given Evan et al.’s close scrutiny of the matter, and being unable to find newer information that might justify the use of a lower nominal value, we have chosen to report the DFT estimates based on the GW recommendation.

As an alternate means of checking our concern about the systematic bias inherent in the DFT method due to the use of HN_3 as a reactant in all of the isodesmic reaction schemes, consideration was given to employing an azide-functionalized molecule other than HN_3 as a reactant. However, we do not believe that any has a $\Delta_f H_g^0(298)$ value more reliable than HN_3 . Nor will the product needed to complement an alternate reactant have a $\Delta_f H_g^0(298)$ more reliable than H_2 . Thus, we did not attempt to obtain $\Delta_f H_g^0(298)$ estimates via the characterization of $\Delta_r H_g^0(298)$ for alternate isodesmic reactions.

Beyond addressing concerns about bias in the various $\Delta_f H_g^0(298)$ estimation methods, other aspects of the results in tables 1 and 2 are notable. For one, they attest to the ability of all of the methods to correctly order the energies of *anti* and *gauche* azide conformations. RM only present G2 results for one azidoethane conformer. Based on the H^0 value they report, they appear to have characterized the *anti* conformer. Based on spectroscopic studies, Nielsen et al. (1998) concluded that the *gauche* conformer of azidoethane was slightly lower in energy than the *anti* conformer in both an N_2 matrix (by 0.13 kcal/mol) and in liquid azidoethane (by 0.03 kcal/mol). The DFT and G2 methods predict both the energy ordering and the small energy difference. The RPH AE model predicts the same energy ordering, but the energy the difference it predicts is larger (0.9 kcal/mol). The better agreement between the DFT estimates and experimentally derived results indicates that results based on B3LYP/6-311++G(d,p) //B3LYP/6-31G(d) calculations are more accurate than those based on B3LYP/6-31G(d) calculations. The results also indicate that the -C-C-N-N- dihedral angle constructed for the calculation of an azide molecule’s $E(i)$ is not a significant consideration if the DFT method is employed, but if the RPH AE model is employed, failure to properly consider it could produce errors up to 1 kcal/mol/primary-azide-group.

As previously noted, the $\Delta_f H_g^0(298)$ estimates for 1-azido-2-methylpropane and 2-azido-2-methylpropane indicate that an isomer with a tertiary azide group will have a $\Delta_f H_g^0(298)$ value about 4 kcal/mol lower than its primary counterpart. This conclusion is supported by the DFT estimates for 1-azido-3-ethylpentane and 3-azido-3-ethylpentane, where the same difference is observed. Similarly, comparison of the results for 1-azidopropane and 2-azidopropane indicate that the $\Delta_f H_g^0(298)$ value for an isomer with a secondary azide group will be from 2–4 kcal/mol lower than that of its primary counterpart. These findings are considered in the analysis of the results from the modified RPH AE model that is to be presented.

As also noted, the results support long-held suspicions (Evans et al., 1959) about the precision claimed by Fagley and Myers (FM) (1954) for their experimentally derived $\Delta_f H_l^0(298)$ values for azidocyclopentane and azidocyclohexane. However, being the only azide compounds with $\Delta_f H_l^0(298)$, $\Delta H_v(298)$, and $\Delta_f H_g^0(298)$ values listed in a prominent reference (Pedley et al., 1986), their reliability is an issue that continues to arise in discussions of azide compound $\Delta_f H_g^0(298)$ values. Calculating $\Delta_f H_g^0(298)$ values for azides from empirically computed bond enthalpies, and finding good agreement with most of their own data, Pepkin and coworkers consider FM's experimentally derived $\Delta_f H_g^0(298)$ values for azidocyclopentane and azidocyclohexane to be ~ 9 and 15 kcal/mol, respectively, too negative (Pepkin et al., 1993). RM called the FM results into question because the $\Delta_f H_g^0(298)$ values for 1-azidoadamantane, 3-azido-3-ethylpentane, and 2-azido-2-phenylpropane that they determined from enthalpy-of-hydrogenation measurements were nearly 20 kcal/mol higher than the $\Delta_f H_g^0(298)$ value estimated from a group energy treatment based on the FM data (Rogers and McLafferty, 1995). However, RM considered their enthalpy-of-hydrogenation measurements "difficult and (perhaps suffering) systematic error" and noted the possible lack of correspondence between the $\Delta_f H_g^0(298)$ values of primary and tertiary azides. Thus, they did not go as far as Pepkin et al. in questioning the FM data.

Despite the many published warnings about the FM data's reliability, one of the few papers to publish an experimentally derived $\Delta_f H^0(298)$ value for an azide-functionalized compound since 1995 employs the data as a basis for calculating the enthalpy of a C-N₃ bond when the carbon atom is in a saturated ring (Finch et al., 1997). And more recently, Liebman (1999), while acknowledging questions about FM's value for azidocyclohexane's $\Delta_f H^0(298)$, still employs it as a basis for assessing whether acyl azides are resonance stabilized. If the DFT estimate for azidocyclohexane is employed instead of the FM datum, the resonance energy (as defined by Liebman) becomes 28.2 kcal/mol. Even if (as might be argued on the basis of results presented in figure 3) the DFT estimate is as much as 3 kcal/mol too high, the resulting value (25.2 kcal/mol) is still too high to be consistent with Liebman's expectation and finding that it falls between those for acyl halides (1.8 kcal/mol) and acyl amides (15.3 kcal/mol) or acyl esters (18 kcal/mol). This, in turn, calls into question his conclusion that a carboxylic acid's rate of amidolysis is inversely proportional to the resonance stabilization criterion that he proposes.

In the course of considering Liebman's study, an alternate generic isodesmic scheme that can be used to compare the relative resonance stabilization of acyl derivatives was identified. It is



By using it in lieu of the scheme employed by Liebman, the calculations would be based on what is certainly a more extensive and reliable $\Delta_f H^0(298)$ database, and they would therefore be a better test of Liebman's hypothesis.

4.1.2 Enthalpies-of-Vaporization

Table 4 compares experimentally derived $\Delta H_v(298)$ values with $\Delta H_v(298)$ estimates obtained via (1) the RPH $\Delta H_v(298)$ model and (2) MD simulations. In all but two of 17 cases, the RPH $\Delta H_v(298)$ estimate is higher than the corresponding experimentally derived value. And for the 15 cases in which both an RPH $\Delta H_v(298)$ estimate and an estimate based on MD was obtained, the RPH $\Delta H_v(298)$ estimate is higher; the differences ranging from nearly 4 kcal/mol for smaller molecules to less than 1 kcal/mol for larger molecules.

Table 4. RPH $\Delta H_v(298)$ model estimates (kcal/mol) compared to experimentally derived values and MD-based estimates.

Compound	$\Delta H_v(298)$ RPH	$\Delta H_v(298)$ exp	Δ RPH-exp	$\Delta H_v(298)$ MD	Δ RPH-MD
Hydrogen azide	7.0	7.3 ^a	-0.3	—	—
1-Azidobutane	11.7	9.2 ^b	2.5	8.7 ^f	3.0
1-Azidopentane	13.2	10.0 ^b	3.2	9.9 ^f	3.3
1-Azidohexane	14.6	11.2 ^b	3.4	11.0 ^f	3.6
1-Azidoheptane	15.8	12.1 ^b	3.7	—	—
1-Azidooctane	17.1	12.8 ^b	4.3	13.3 ^f	3.8
1,3-Diazidopropane	13.9	11.2 ^b	2.7	12.7 ^f	1.2
1,4-Diazidobutane	15.0	12.4 ^b	2.6	13.8 ^f	1.2
1,5-Diazidopentane	16.3	13.6 ^b	2.7	14.9 ^f	1.4
1,6-Diazidohexane	17.1	14.6 ^b	2.5	15.6 ^f	1.5
1,8-Diazidooctane	19.1	—	—	17.5	1.6
2-Azido-N-methylethanamine	11.8	—	—	11.2	0.6
2-Azido-N-cyclopropylethanamine	13.9	—	—	12.2	1.7
2-Azido-N,N-dimethylethanamine	11.9	9.4 ^c	2.5	10.5	1.4
1-(2-Azidoethyl)pyrrolidine	13.5	—	—	12.5	1.0
Bis(2-azidoethyl)ethanamine	16.3	—	—	15.6	0.7
2-Azidoethanol	12.6	—	—	12.1	0.5
Azidotrinotromethane	11.9	11.0 ^d	0.9	—	—
1-Azido-1,1-dinitroethane	13.0	13.5 ^d	-0.5	—	—
Azidobenzene	11.2	10.7 ^d	0.5	—	—
Azidomethylbenzene	13.6	11.5 ^d	2.1	—	—
Azidocyclopentane	11.3	10.0 ^e	1.3	—	—
Azidocyclohexane	11.8	11.0 ^e	0.8	—	—

^aAttributed to Gunther et al. (1935) by Gray and Waddington (1956).

^b(Lee et al., 1989).

^c(Dee, 2000).

^d(Pepkin et al., 1993).

^e(Fagley and Myers, 1954).

^f(McQuaid et al., 2004).

Although these comparisons suggest that the RPH $\Delta H_v(298)$ estimates are too high, the magnitude of the bias is arguable. Nine of the cases considered involve straight-chain alkyl azides whose experimentally derived $\Delta H_v(298)$ values were determined by Lee and coworkers

(1989). The possibility that those values are systematically low was noted in the course of developing COMPASS force field parameters for azide atom types (McQuaid et al., 2004). Finding that all MD-based $\Delta H_v(298)$ estimates obtained from simulations that reproduced these compounds' densities were higher than the values reported by Lee et al., the reliability of the Lee et al. values was questioned. Specifically, it was noted that Lee et al. had derived the values from vapor pressure measurements obtained at temperatures higher than 298 K. Another instance where this technique appears to yield a low $\Delta H_v(298)$ value is 2-azido-N,N-dimethylethanamine (DMAZ). In its case, the experimentally derived $\Delta H_v(298)$ value (9.4 kcal/mol) was obtained from an equation fit to vapor pressure data at temperatures from 293 to 433 K (Dee, 2000). But Dee notes that that equation does not well estimate DMAZ's vapor pressure at temperatures less than 313 K. Moreover, if the Clausius-Claperyon equation is fit to the DMAZ vapor pressure data at 293 K, 298 K, and 303 K (only), $\Delta H_v(298)$ is calculated to be 14.4 kcal/mol. Thus, the 11.9 kcal/mol value predicted for $\Delta H_v(\text{DMAZ}, 298)$ by the RPH $\Delta H_v(298)$ model may not be too high.

Besides the 10 cases noted, the experimentally derived $\Delta H_v(298)$ values for four other compounds in table 4 were derived from measurements of vapor pressure at temperatures higher than 298 K: azidobenzene, azidomethylbenzene, azidotritromethane, and 1-azido-1,1-dinitroethane (Pepkin et al., 1993). Thus, it is considered that 14 of the 17 experimentally derived $\Delta H_v(298)$ values in table 4 may be lower than their actual value. In addition to this concern, the experimentally derived $\Delta H_v(298)$ values for azidocyclopentane and azidocyclohexane, which were derived from surface tension measurements via an empirically-based equation, were considered by its authors to be "approximate" (Fagley and Myers, 1954). All told, none of the experimentally derived $\Delta H_v(298)$ values in table 4 are completely trusted, and most could well be too low.

In addition to the experimentally derived $\Delta H_v(298)$ values for 2-azidoethanol listed in table 4, estimates for its value have been published (Finch et al., 1997; NIST Chemistry Web Book, 2005; Pepkin et al., 1993). One estimate is based on the measured $\Delta H_v(298)$ value of 2-chloroethanol (11.0 kcal/mol) (Finch et al., 1997; NIST Chemistry Web Book, 2005). The similarity between azide and chloride analog $\Delta H_v(298)$ values has previously been noted (Lee et al., 1989; McQuaid, 2002), and the RPH $\Delta H_v(298)$ estimate (12.6 kcal/mol) and the estimate derived from MD simulations (12.1 kcal/mol) compare favorably to 2-chloroethanol's value. Using a method developed by Chironov and coworkers (1984), Pepkin et al. (1993) estimate 2-azidoethanol's $\Delta H_v(298)$ to be 16.5 kcal/mol. Based on the other estimates reported, that estimate appears to be too high.

Given the bias suspected in much of the experimentally derived $\Delta H_v(298)$ values, the "approximate" nature of some of the others, and the indications that the RPH $\Delta H_v(298)$ model estimates were reasonable, we decided against re-parameterizing it with a training set more heavily weighted with azide-compound data. Results presented in the next section provide additional justification for that decision.

4.2 Parameter Addition to the RPH AE Model

4.2.1 The RPH-M AE Model

Since the experimentally derived $\Delta_f H_g^0(298)$ values for azidocyclopentane and azidocyclohexane are believed to be too negative, and cyanogen azide's experimentally derived $\Delta_f H_g^0(298)$ value not only too negative, but associated with a bonding scheme unlike any found in any other molecule, only 12 of the carbon-containing compounds in table 1 were considered to have reliable and relevant experimentally derived $\Delta_f H_g^0(298)$ values. Considered too small a set for the desired parameterization, it was supplemented with $\Delta_f H_g^0(298)$ values that were calculated from experimentally derived $\Delta_f H_l^0(298)$ or $\Delta_f H_s^0(298)$ values and RPH enthalpy-of-phase-change estimates. Shown in table 5, the complete set consists of (1) eight experimentally derived $\Delta_f H_g^0(298)$ values, (2) eight $\Delta_f H_g^0(298)$ values derived from experimentally derived $\Delta_f H_l^0(298)$ values and RPH $\Delta H_v(298)$ estimates, and (3) eight $\Delta_f H_g^0(298)$ values derived from experimentally derived $\Delta_f H_s^0(298)$ values and RPH $\Delta H_s(298)$ estimates. The only experimentally derived $\Delta_f H^0(298)$ values that were found in the literature search and not employed in the fit were those previously questioned (cyanogen azide, azidocyclopentane, and azidocyclohexane) and an azidotriazole compound (5-methyl-4-amino-3-azidotriazole) whose value was questioned by the authors who published it (Denault et al., 1968).

Fitting equation 1 to the 24-compound set of “experimentally derived” $\Delta_f H_g^0(298)$ values, the azide-group equivalent [$\varepsilon(N_3)$] was determined to be -164.309969 hartrees. This value is 0.0123 hartrees (7.7 kcal/mol) more positive than the value obtained by multiplying the N'-atom equivalent [$\varepsilon(N')$] of the RPH AE model by 3. In other words, the energy required to dissociate an azido group into 3 N atoms—i.e., the group's average bond dissociation energy—is 7.7 kcal/mol lower than the expectation based on equating azido group N atoms with the N' atoms in RPH's training set. Consequently, $\Delta_f H_g^0(298)$ estimates based on the RPH-M AE model are/will be 7.7 kcal/mol/azido-group lower than those based on the RPH AE model.

To assess the applicability of the RPH $\Delta H_v(298)$ and $\Delta H_s(298)$ estimation models for use in predicting those properties for azide-functionalized compounds, $\varepsilon(N_3)$ values derived by fitting equation 1 to (1) various subsets of the $\Delta_f H_g^0(298)$ training set data and (2) $\Delta_f H_g^0(298)$ values determined via the DFT method were compared to the value derived from the entire set. If the 8-compound set of $\Delta_f H_g^0(298)$ values is employed to derive $\varepsilon(N_3)$, its value is 0.0013 hartrees (0.8 kcal/mol) lower than the one derived from the entire set. Similarly, if the 8-compound [$\Delta_f H_l^0(298) + \Delta H_v(298)$] set is employed to derive $\varepsilon(N_3)$, its value is 0.0004 hartrees (0.2 kcal/mol) more positive than the one derived from the entire set. And if the 8-compound [$\Delta_f H_s^0(298) + \Delta H_s(298)$] set is employed, its value is 0.00006 hartrees (0.0 kcal/mol) more positive than the one derived from the entire set. If equation 1 is fit to the 19 DFT $\Delta_f H_g^0(298)$ estimates reported in table 5, the $\varepsilon(N_3)$ derived is only 0.0015 hartrees (0.9 kcal/mol) more positive than the one derived from the entire set. These results suggest that the RPH $\Delta H_v(298)$

Table 5. $\Delta_f H^0(298)$ estimates compared to experimentally derived $\Delta_f H^0(298)$ values (kcal/mol).

Compound	ΔH_v	ΔH_s	$\Delta_f H_s^0$		$\Delta_f H^0$	$\Delta_f H^0$	Δ	$\Delta_f H^0$	Δ
			RPH-M	DFT	Exp.	RPH-M AE		DFT	
Hydrogen azide (g)	—	—	75.7	—	71.7 ^a	75.7	4.0 ^l	—	—
3-Azido-3-ethylpentane (g)	—	—	40.8	39.7	40.6 ^b	40.8	0.2	39.7	-0.9
1-Azidoadamantane (g)	—	—	59.5	50.8	51.6 ^b	59.5	7.9	50.8	-0.8
2-Azido-2-phenylpropane (g)	—	—	81.7	86.4	87.4 ^b	81.7	-5.7	86.4	-1.0
Cyanogen azide (g)	—	—	122.4	122.7	108.0 ^c	122.4	14.4 ^l	122.7	14.7
1-Azidopentane (g)	—	—	49.8	52.7	49.3 ^d	49.8	0.5	52.7	3.4
1-Azidohexane (g)	—	—	44.8	47.7	40.8 ^d	44.8	4.0	47.7	6.9
1-Azidoheptane (g)	—	—	39.7	42.8	44.9 ^d	39.7	-5.2	42.8	-2.1
1-Azidooctane (g)	—	—	34.7	37.9	40.2 ^d	34.7	-5.5	37.9	-2.3
2-Azido-N,N-dimethylethanamine (g)	—	—	76.8	79.9	78.7 ^e	76.8	-1.9	79.9	1.2
1-(2-Azidoethyl)-pyrrolidine (l)	13.5	—	80.5	68.7	72.8 ^e	67.0	-5.8	68.7	-4.2
Bis(2-azidoethyl) methanamine (l)	16.3	—	158.9	164.8	139.9 ^e	142.6	2.7	148.5	8.6
2-Azidoethanol (l)	12.6	—	39.9	33.0	22.5 ^f	27.3	4.8	20.4	-2.1
Azidotritromethane (l)	11.9	—	88.5	90.2	73.2 ^g	76.6	3.4	76.6	3.4
1-Azido-1,1-dinitroethane (l)	13.0	—	62.5	63.4	46.9 ^g	49.5	2.6	50.4	0.5
Azidobenzene (l)	11.2	—	101.0	102.8	82.3 ^h	89.8	7.5	91.6	9.3
Azidomethylbenzene (l)	13.4	—	101.2	102.0	88.0 ^g	87.8	-0.2	88.6	0.6
Ethylazidoacetate (l)	13.8	—	-13.5	-14.5	-33.3 ^h	-27.3	6.0	-28.3	5.0
Azidocyclopentane (l)	11.3	—	66.7	67.0	42.8 ⁱ	55.4	12.6 ^l	55.7	12.9
Azidocyclohexane (l)	11.8	—	55.3	56.2	25.9 ⁱ	43.5	17.6 ^l	44.4	18.9
3-Azidotriazole (s)	—	26.5	135.3	—	105.2 ^j	108.8	3.6	—	—
4-Amino-3-azidotriazole (s)	—	26.0	166.4	—	136.5 ^j	140.4	3.9	—	—
5-Methyl-3-azidotriazole (s)	—	27.4	123.3	—	93.8 ^j	95.9	2.1	—	—
5-Methyl-4-amino-3-azidotriazole (s)	—	28.0	154.3	—	115.8 ^j	126.2	10.4 ^l	—	—
5-Ethyl-3-azidotriazole (s)	—	29.8	118.5	—	87.4 ^j	88.7	1.3	—	—
5-Ethyl-4-amino-3-azidotriazole (s)	—	31.0	149.5	—	118.5 ^j	118.5	0.0	—	—
5-Phenyl-3-azidotriazole (s)	—	33.6	155.4	—	127.2 ^j	121.8	-5.4	—	—
5-Phenyl-4-amino-3-azidotriazole (s)	—	35.6	188.1	—	159.5 ^j	152.5	-7.0	—	—
4-Azidonitrobenzene (s)	—	22.2	93.1	—	73.8 ^k	70.9	-1.9	—	—

^a(Gray and Waddington, 1956).^b(Wayne and Snyder, 1993).^c(Okabe and Mele, 1969).^d(Murrin and Carpenter, 1957).^e(Thompson, 2000).^f(Fagley et al., 1953).^g(Pepkin et al., 1993).^hAttributed to Roth and Mueller (1929) by Pepkin et al. (1993).ⁱ(Fagley and Myers, 1954).^j(Denault et al., 1968).^k(Finch et al., 1997).^lNot employed in the RPH-M AE model parameterization.

and $\Delta H_s(298)$ estimation models yield reasonably accurate estimates for azides, and no further consideration was given to developing new ones from training sets more heavily weighted with azide compounds.

4.2.2 Estimates for ARDEC-Synthesized Compounds

Table 6 presents the RPH-M AE and DFT model $\Delta_f H_g^0(298)$ estimates for the ARDEC-synthesized compounds. In all cases except [8] and [9], the two approaches yield estimates that are within 10 kcal/mol of one another. It is also observed that the DFT estimates tend to be higher than the RPH-M AE estimates.

Table 6. $\Delta_f H_g^0(298)$, $\Delta H_s(298)$, and $\Delta_f H_s^0(298)$ estimates for ARDEC-synthesized compounds (kcal/mol).

Compound	$\Delta_f H_g^0(298)$		$\Delta H_s(298)$	$\Delta_f H_s^0(298)$	
	RPH-M AE	DFT	RPH	RPH-M AE	DFT ^a
[1]	315.6	324.2	29.2	286.4	295.0
[2]	195.7	194.1	26.0	169.8	168.1
[3]	215.8	225.0	29.8	186.0	195.2
[4]	149.7	159.3	23.4	126.3	135.9
[5]	302.0	307.8	41.0	261.0	266.8
[6]	504.5	500.5	229.1	275.3	271.4
[7]	481.7	491.0	131.4	350.3	359.6
[8]	815.1	840.8	359.6	455.6	481.2
[9]	637.4	662.0	388.7	248.7	273.3

^aRecommended nominal values.

An analysis of the results points to some likely sources for the differences in the models' estimates. One fairly certain source of the differences is related to the fact that, except for the one tertiary group in [1], all of the azide groups in the ARDEC-synthesized compounds are primary groups. As noted in the previous discussion, for a given stoichiometry, the $\Delta_f H_g^0(298)$ of isomers with primary groups are expected to be 2–4 kcal/mol higher than isomers with secondary or tertiary groups. Since the 24-compound training set employed for the parameterization of the RPH-M AE model contains 12 molecules with primary groups and 12 molecules with secondary or tertiary groups, the RPH-M AE model's $\Delta_f H_g^0(298)$ predictions are expected to be negatively biased 1–2 kcal/mol/primary-group and positively biased 1–2 kcal/mol/secondary- or tertiary-group. Therefore, it is expected, for example, that the RPH-M AE model's prediction for [1] will be negatively biased 2–4 kcal/mol while its estimates for [8] and [9] will be negatively biased 12–24 kcal/mol. Thus, this consideration alone can account for most of the differences observed between the RPH-M AE and DFT estimates (see table 7).

Table 7. Expected bias in RPH-M AE model estimates.

Compound	No. of Primary Groups		No. of Tertiary Groups	Bias Estimate ^a
	<i>anti</i>	<i>gauche</i>		
[1]	1	2	1	-4.5
[2]	1	2	—	-6
[3]	1	2	—	-6.5
[4]	—	2	—	-7
[5]	2	—	—	-3
[6]	2	6	—	-18
[7]	2	4	—	-13
[8]	4	8	—	-26
[9]	7	5	—	-23

^aAssumes estimates for primary groups are 2 kcal/mol negatively biased, estimates for tertiary groups are positively biased 2 kcal/mol, estimates for *gauche* configurations are negatively biased 0.5 kcal/mol, and estimates for *anti* configurations are positively biased 0.5 kcal/mol.

Another source of difference between the RPH-M AE model and the DFT method estimates is the difference in their underlying QM-models' results for *anti* and *gauche* orientations of primary azido groups. As noted, the results of spectroscopic studies indicate azidoethane's *gauche* conformer to be about 0.1 kcal/mol lower in energy than its *anti* conformer. Both the RPH-M AE model and the DFT method predict the energy ordering found experimentally, but the DFT method [based on B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) results] predicts the small energy difference observed while the RPH-M AE model [based on B3LYP/6-31G(d) results] predicts a larger (0.9 kcal/mol) difference. In the case of the DFT method, this suggests that even if this structural consideration is not properly accounted for, its potential to produce errors is minimal. (We have, however, attempted to mitigate the potential for error by "matching" the product and reactant structures used for the isodesmic reactions upon which the calculations are based.) In the RPH-M AE model, on the other hand, neglect of this consideration has the potential to produce errors up to 0.9 kcal/mol/primary-azido-group, with the magnitude and sign of the error depending on (1) the number of *anti* and *gauche* configurations specified in the training set and (2) the configuration constructed for the calculation of $E(i)$ of the molecule of interest.

Of the 10 compounds in the training set that have primary azido groups whose *anti* or *gauche* configurations are distinguishable, 6 *anti* configurations and 4 *gauche* configurations were built. Therefore, our expectation is that $\Delta_f H_g^0(298)$ estimates calculated from $E(i)$ values for structures with *gauche* configurations will be negatively biased about 0.5 kcal/mole-configuration while predictions obtained from structures with *anti* configurations will be positively biased about 0.5 kcal/mole-configuration. The RPH-M $\Delta_f H_g^0(298)$ estimates reported in table 6 have not been corrected to reflect this expectation.

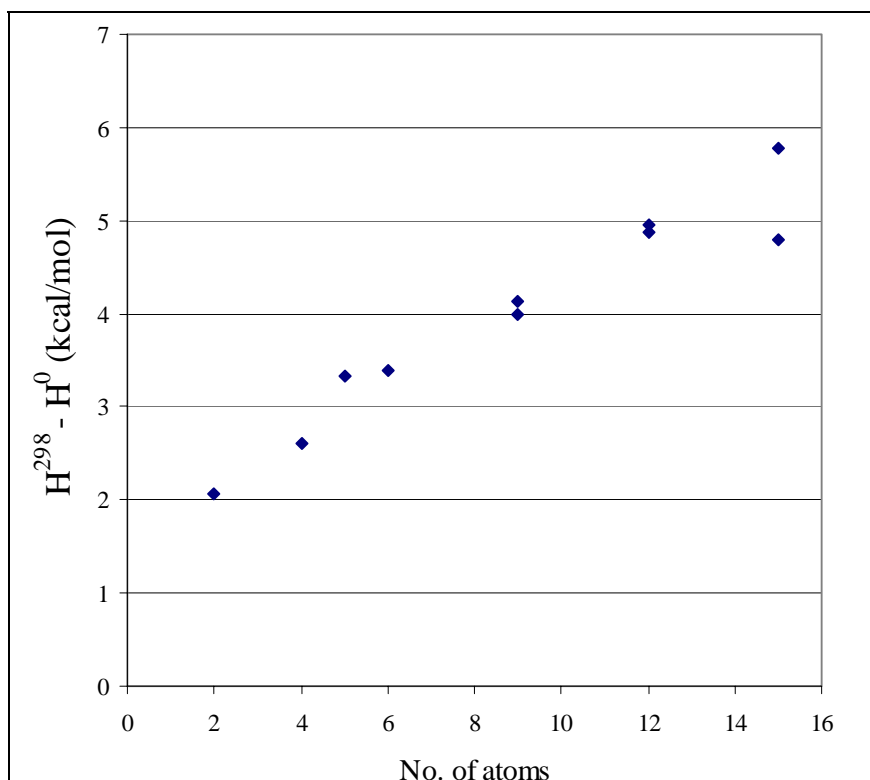


Figure 7. The magnitude of ΔH contributions to azide enthalpy-of-formation values.

The calculation of the $\Delta H(i)$ contribution to $\Delta_f H_g^0(298)$ included in the estimates was another potential source of error that we considered. As shown in figure 7, which presents results based on B3LYP/6-31G(d) calculations, the contribution of $\Delta H(i)$ to $\Delta_f H_g^0(298)$ is nonnegligible and the contribution increases with the number of atoms in the molecule. In the case of the DFT method, $\Delta H(i)$ values (like those in figure 7) are calculated based on B3LYP/6-31G(d) normal mode calculations. Such calculations are known to poorly describe low frequency modes, and large molecules have a large number of such modes. In addition, the enthalpic contributions of modes associated with hindered internal rotation are slightly smaller than has been assumed in the calculations. However, such deficiencies are found in the $\Delta H(i)$ calculations of both reactants and products. Therefore, we expect the systematic error in the DFT method estimates due to this consideration to be negligible.

The possibility that the RPH-M AE model might be incorrectly estimating the $\Delta H(i)$ contribution to a molecule's $\Delta_f H_g^0(298)$ is not as easily dismissed. Though the development of an AE model does not involve the calculation of atomization enthalpies (as does the G2-ae method), the $\Delta H(i)$ contribution to $\Delta_f H_g^0(298)$ that is “incorporated” into an atom-equivalent can be understood by reference to such a calculation. The $\Delta_f H_g^0(298)$ of a compound with stoichiometry $C_a H_b N_c O_d$ is defined with respect to a reference state. (The details of the reference

state are immaterial to this discussion.) The $H(298)$ of $C_aH_bN_cO_d$ at 298 K includes contributions due to (1) $E(i)$, (2) $ZPVE(i)$, and (3) $\Delta H(i)$. That is,

$$H(C_aH_bN_cO_d, 298) = E(C_aH_bN_cO_d) + ZPVE(C_aH_bN_cO_d) + \Delta H(C_aH_bN_cO_d). \quad (9)$$

Similarly, the enthalpy of the atomized state of this stoichiometry ($aC+bH+cN+dO$) may be written

$$\begin{aligned} H(aC + bH + cN + dO, 298) = & a(E(C, 298) + \Delta H(C, 298)) + b(E(H, 298) + \Delta H(H, 298)) \\ & + c(E(N, 298) + \Delta H(N, 298)) + d(E(O, 298) + \Delta H(O, 298)). \end{aligned} \quad (10)$$

(Atoms have no ZPVE.) By definition,

$$\Delta_f H(C_aH_bN_cO_d, 298) = H(C_aH_bN_cO_d, 298) - H(\text{ref. state}, 298) \quad (11)$$

and

$$H(\text{ref. state}, 298) = \sum_j n(j)[H(j, 298) - \Delta_f H^0(j, 298)]. \quad (12)$$

We may therefore write

$$\begin{aligned} \Delta_f H^0(C_aH_bN_cO_d, 298) = & E(C_aH_bN_cO_d) + ZPVE(C_aH_bN_cO_d) + \Delta H(C_aH_bN_cO_d) \\ & - \sum_j n(j)[H(j, 298) - \Delta_f H^0(j, 298)]. \end{aligned} \quad (13)$$

A comparison of equation 13 with equation 1 suggests writing $\varepsilon(j)$ as

$$\varepsilon(j) = H(j, 298) - \Delta_f H^0(j, 298) - \Delta(j), \quad (14)$$

with $\Delta(j)$ being a parameter that accounts for the shortcomings of the theory in calculating $E(C_aH_bN_cO_d)$ [$\Delta E(C_aH_bN_cO_d)$] and the contributions to $\Delta_f H^0(298)$ of $ZPVE(C_aH_bN_cO_d)$ and $\Delta H(C_aH_bN_cO_d)$. That is,

$$\Delta(j) = \Delta E(C_aH_bN_cO_d) + ZPVE(C_aH_bN_cO_d) + \Delta H(C_aH_bN_cO_d). \quad (15)$$

To obtain a sense for the magnitude of $\Delta(j)$, the case of H_2 is instructive. The RPH(-M) AE model predicts $\Delta_f H_g^0(H_2, 298)$ to be 5.4 kcal/mol while its defined value is 0.0 kcal/mol. Substituting into equation 15 the value for the atom-equivalent for H atoms [$\varepsilon(H) = -0.592039$ hartrees], an H atom's electronic energy [$E(H) = -0.500000$ hartrees], and established values for ΔH (1.48 kcal/mol) and $\Delta_f H_g^0(298)$ (52.1 kcal/mol), $\Delta(H)$ is found to be -7.1 kcal/mol. In other words, the magnitude of the empirical correction included in the RPH(-M) AE model estimation of $\Delta_f H_g^0(H_2, 298)$ is 14.2 kcal/mol.

Computing $\Delta_f H_g^0(H_2, 298)$ using (1) the B3LYP/6-31G(d)-calculated electronic energy for H_2 [$E(H_2) = -1.175482$ hartrees], (2) H_2 's spectroscopically determined ZPVE (6.23 kcal/mol), and

(3) an established value for $\Delta H(298)$ (2.02 kcal/mol), a value of -0.6 kcal/mol is obtained. If this value is representative of B3LYP/6-31G(d)'s deficiency in computing $E(i)$, then the portion of $\Delta(H)$ that accounts for the deficiency is -0.3 kcal/mol. Making this assumption, the discrepancy between the accepted value for $\Delta_f H_g^0(H_2, 298)$ and its prediction via the RPH-M AE model is attributable to the model predicting too large a $\Delta H(298)$ contribution to $\Delta_f H_g^0(H_2, 298)$. That is, the model is indicated as specifying a $\Delta H(298)$ contribution of 13.6 kcal/mol (or 6.8 kcal/mole/H-atom) while the actual $\Delta H(298)$ contribution is 8.25 kcal/mol.

H atoms in molecules with three or more atoms have more degrees of freedom than the H atoms of H_2 . (In H_2 they are limited to translation, rotation, and a bond stretching mode. In larger molecules they are involved in angular and torsional vibrational modes as well.) As a result, the H atoms in molecules with three or more atoms will make larger per atom thermal energy contributions to their molecules than the H atoms of H_2 . Since all of the molecules employed in parameterizing the RPH(-M) AE model $\varepsilon(H)$ have more than three atoms, the RPH-M AE model's overprediction of $\Delta_f H_g^0(H_2, 298)$ is consistent with expectations. If the thermal contributions of individual atom types are derived from a least squares fit of the thermal enthalpies calculated for the 16 azido compounds characterized via the DFT method, a value of 6.1 kcal/mol is obtained for H atoms. This value is comparable to the 6.8 kcal/mol value indicated by the analysis summarized in the previous paragraph. Although this agreement is reassuring, it will be appreciated that, being an additive contribution, small discrepancies between empirically derived and actual thermal contributions for a given atom type can lead to large errors in a molecule with a large number of a given atom type. For example, compound [9] has 36 H atoms. Therefore, a discrepancy as small as 0.1 kcal/mol (0.00016 hartrees) will produce a 3.6 kcal/mol error in the RPH(-M) AE model estimate for it.

The previous analysis clearly indicates that the DFT $\Delta_f H_g^0(298)$ estimates are much less likely to have significant systematic error in them than the RPH-M AE estimates. Thus, they are our recommendation for use as nominal $\Delta_f H_g^0(298)$ values for compounds [1] – [9]. Based on the validation work, the DFT $\Delta_f H_g^0(298)$ estimates are considered likely to be within $+10/(-10-1.4n)$ kcal/mol of their actual value, where n in the lower bound is the number of azido groups in the molecule. The larger lower bound is specified based on our concern that the $\Delta_f H_g^0(HN_3, 298)$ value we have employed in deriving the DFT $\Delta_f H_g^0(298)$ estimates may be as much as 1.4 kcal/mol too high.

Finding no experimentally derived $\Delta H_s(298)$ values for azide-functionalized compounds, our assessment of the validity of the RPH $\Delta H_s(298)$ estimates for this class of compounds is speculative. [However, it should be recognized that this issue is not restricted to azide-functionalized compounds. As noted by J. A. Martinho Simões in introducing the Organometallic Thermochemistry Database of the NIST Chemistry Web Book (2005), there is no general method for estimating $\Delta H_s(298)$ for most classes of compounds, so reported $\Delta H_s(298)$ values are often unreliable.] $\Delta H_s(298)$ estimates for compounds [1] – [5] are comparable to estimates for the similarly sized triazoles employed to establish $\varepsilon(N_3)$ for the

RPH-M AE model. Based on: (1) the spread in the $\Delta H_s(298)$ estimates for the triazoles and compounds [1] – [5] and (2) the agreement between experimentally derived $\Delta_f H_s^0(298)$ values and the $\Delta_f H_s^0(298)$ estimates [which are based in part on the $\Delta H_s(298)$ estimates], we expect the $\Delta H_s(298)$ estimates for compounds [1] – [5] to be within ± 5 kcal/mol of their actual value. The $\Delta H_s(298)$ estimates for compounds [6] – [9] are considerably higher than all of the other compounds whose $\Delta H_s(298)$ values were estimated. Given their large size, high values were expected. However, for these four compounds we consider there to be insufficient information to assign meaningful error limits.

5. Summary

Semi-empirical models that were parameterized by RPH for use in predicting $\Delta_f H_g^0(298)$ and $\Delta H_s(298)$ values for energetic materials were evaluated for use in obtaining $\Delta_f H_s^0(298)$ estimates for a set of polyazido compounds that were synthesized by ARDEC. Not unexpectedly, the RPH AE model for estimating $\Delta_f H_g^0(298)$ was found to underpredict the quantity for azide-functionalized compounds. An equivalent for azide groups [$\mathcal{E}(\text{N}_3)$] was therefore added to the model, its value determined by fitting the RPH AE model and the added parameter to a $\Delta_f H_g^0(298)$ database for azide-functionalized compounds that was constructed from a literature search. For azide compounds with less than 30 atoms, $\Delta_f H_g^0(298)$ estimates obtained via the revised (RPH-M AE) model compare well with estimates derived from B3LYP/6-311++G(d,p)//B3LYP/6-31G(d)-calculated enthalpies-of-reaction for isodesmic reactions. However, differences become significant for larger molecules. Those differences appear to be attributable to biases in the RPH-M AE model. The B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) estimates are thus considered more reliable. No experimentally derived $\Delta H_s(298)$ values for azide compounds could be found to validate the RPH $\Delta H_s(298)$ model estimates, but azide compound $\Delta_f H_s^0(298)$ estimates derived from $\Delta_f H_g^0(298)$ and $\Delta H_s(298)$ estimates are in good agreement with experimentally derived values. This suggests that the RPH $\Delta H_s(298)$ estimates are reasonable. Based on the validation effort, we are confident that $\Delta_f H_s^0(298)$ estimates based on B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) $\Delta_f H_g^0(298)$ estimates and RPH $\Delta H_s(298)$ estimates are reasonable for the nine ARDEC-synthesized compounds, but the error limits placed on them are speculative.

6. References

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Appendix. Supporting Information

This appendix provides the data employed in the calculations whose results are reported in the main body of this report. Included are quantum mechanics results and thermochemical properties identified via a literature search. The source of the thermochemical property data is also provided.

Table A-1. Training and validation set data: Atom typing and B3LYP-calculated energies and enthalpies.

Compound	Number of Specified Atom Type								E^0	$ZPVE+\Delta H$	E^0	$H(298)$
									6-31G(d)	6-31G(d)	6-311++G(d,p)	^a
	C	H	N	O	C'	N'	O'	N ₃	hartrees			
Hydrogen azide	0	1	0	0	0	0	0	1	-164.782283	0.025594	-164.835790	-164.810196
Azidomethane	1	3	0	0	0	0	0	1	-204.093313	0.056061	-204.153161	-204.097100
<i>gauche</i> -Azidoethane	2	5	0	0	0	0	0	1	-243.410757	0.085959	-243.481460	-243.395501
<i>anti</i> -Azidoethane	2	5	0	0	0	0	0	1	-243.409060	0.085972	-243.481460	-243.395488
1-Azidopropane	3	7	0	0	0	0	0	1	-282.724571	0.115927	-282.805854	-282.689927
2-Azidopropane	3	7	0	0	0	0	0	1	-282.728133	0.115393	-282.809331	-282.693938
1-Azidobutane	4	9	0	0	0	0	0	1	-322.038218	0.145923	-322.130180	-321.984257
1-Azidopentane	5	11	0	0	0	0	0	1	-361.351986	0.175839	-361.454609	-361.278770
1-Azidohexane	6	13	0	0	0	0	0	1	-400.665714	0.205793	-400.778969	-400.573176
1-Azidoheptane	7	15	0	0	0	0	0	1	-439.979424	0.235743	-440.103317	-439.867574
1-Azidooctane	8	17	0	0	0	0	0	1	-479.293144	0.265692	-479.427661	-479.161969
1-Azido-3-ethylpentane	7	15	0	0	0	0	0	1	-439.973006	0.235689	-440.096395	-439.860706
3-Azido-3-ethylpentane	7	15	0	0	0	0	0	1	-440.101881	0.234974	-440.100797	-439.866907
1-Azidoadamantane	10	15	0	0	0	0	0	1	-554.312840	0.257888	-554.455536	-554.197648
1,3-Diazidopropane	3	6	0	0	0	0	0	2	-446.302204	—	—	—
1,4-Diazidobutane	4	8	0	0	0	0	0	2	-485.617452	—	—	—
1,5-Diazidopentane	5	10	0	0	0	0	0	2	-524.931376	—	—	—
1,6-Diazidohexane	6	12	0	0	0	0	0	2	-564.245440	—	—	—
1,8-Diazidooctane	8	16	0	0	0	0	0	2	-642.873125	—	—	—
2-Azido-N,N-dimethylethanamine	4	10	1	0	0	0	0	1	-377.369424	0.163875	-377.477199	-377.313324
1-(2-Azidoethyl)pyrrolidine	6	12	1	0	0	0	0	1	-454.790880	0.201640	-454.916466	-454.714826
Bis(2-azidoethyl)methanamine	5	11	1	0	0	0	0	2	-580.262939	0.200190	-580.425489	-580.225299
2-Azidoethanol	2	5	0	1	0	0	0	1	-318.612481	0.091893	-318.717314	-318.625421
Azidotrinitromethane	1	0	0	0	0	3	6	1	-817.5331	0.069254	-817.782074	-817.712820
1-Azido-1,1-dinitroethane	2	3	0	0	0	2	4	1	-652.39168	0.094724	-652.589294	-652.494570
Azidobenzene	0	5	0	0	6	0	0	1	-395.838271	0.111734	-395.942927	-395.831193
Azidomethylbenzene	1	7	0	0	6	0	0	1	-435.143680	0.141792	-435.259955	-435.118163
2-Azido-2-phenylpropane	3	13	0	0	6	0	0	1	-553.091849	0.230621	-553.239230	-553.008611
Azidocyclopentane	5	9	0	0	0	0	0	1	-360.141021	0.153443	-360.239936	-360.086493
Azidocyclohexane	6	11	0	0	0	0	0	1	-399.464881	0.183777	-399.572657	-399.388880
ethylazidoacetate	3	7	0	1	1	0	1	1	-471.281904	0.133502	-471.421906	-471.288404
3-Azidotriazole	0	2	1	0	2	2	0	1	-405.827969	—	—	—
4-Amino-3-azidotriazole	0	3	2	0	2	2	0	1	-461.144422	—	—	—
5-Methyl-3-azidotriazole	1	4	1	0	2	2	0	1	-445.152656	—	—	—
5-Methyl-4-amino-3-azidotriazole	1	5	2	0	2	2	0	1	-539.782789	—	—	—
5-Ethyl-3-azidotriazole	2	6	1	0	2	2	0	1	-484.466020	—	—	—
5-Ethyl-4-amino-3-azidotriazole	2	7	2	0	2	2	0	1	-539.782789	—	—	—
5-Phenyl-3-azidotriazole	0	6	1	0	8	2	0	1	-636.892366	—	—	—
5-Phenyl-4-amino-3-azidotriazole	0	7	2	0	8	2	0	1	-692.206318	—	—	—
4-Azidonitrobenzene	0	4	0	0	6	1	2	1	-600.339498	—	—	—
Cyanogen azide	0	0	0	0	1	1	0	1	-257.002989	0.026257	-257.076218	-257.049961

^a $E^0(6-311+G(d,p))+ZPVE+\Delta H$.

Table A-2. Atom equivalents (hartrees).^a

Atom Type	Equivalent
C	−38.121621
H	−0.592039
N	−54.774096
O	−75.161771
C'	−38.121380
N'	−54.765886
O'	−75.157348
N ₃	−164.310800

^aAll except N₃ came from Rice, B. M.; Pai, S. V.; Hare, J. Predicting the Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. *Combustion and Flame* **2000**, 118, 445–458.

Table A-3. Data for G2-type calculations.

Compound	$\Delta_f H_g^0(298)$	$H(298)$
	kcal/mol	hartrees
C	171.3 ^a	−37.781940
H	52.6 ^a	−0.497639
N	113.0 ^a	−54.515599
O	59.6 ^a	−74.979669
H ₂	0.0 ^a	−1.163046
HCN	32.3 ^a	−93.281429
Methane	−17.9 ^a	−40.407075
Ethane	−20.1 ^b	−79.626397
Propane	−25.0 ^b	−118.850225
Butane	−30.1 ^b	−158.074298
2-Methylpropane	−32.1 ^b	−158.077509
Ethanol	−56.2 ^c	−154.759160
Hydrogen azide	71.66 ^d	−164.556240
Azidomethane	—	−203.770900
<i>gauche</i> -Azidoethane	—	−242.998480
<i>anti</i> -Azidoethane	—	−242.998260
1-Azidopropane	—	−282.222210
2-Azidopropane	—	−282.228460
1-Azidobutane	—	−321.446210
1-Azido-2-methylpropane	—	−321.451400
2-Azido-2-methylpropane	—	−321.459880
2-Azidoethanol	—	−318.128630
Cyanogen azide	—	−256.645040

^aValues are from Chase, M.W., Jr. NIST-JANAF Thermochemical Tables, Fourth Edition. *J. Phys. Chem. Ref. Data, Monograph 9* **1998**, 1–1951.

^bPittam, D.A.; Pilcher, G. Measurements of Heats of Combustion by Flame Calorimetry. Part 8.-Methane, Ethane, Propane, n-Butane and 2-Methylpropane. *J. Chem. Soc. Faraday Trans. 1* **1972**, 68, 2224–2229.

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Table A-4. Data for $\Delta_f H(298)$ calculations.

Compound	$\Delta_f H^\circ(298)$	$E(SCF)$	$ZPE + \Delta H$	$H(298)$
	kcal/mol	B3LYP/6-311++G(d,p)	B3LYP/6-31G(d)	
hartrees				
Hydrogen azide	71.7 ^a	-164.835790	0.025594	-164.810196
H ₂	0.0 ^b	-1.179570	0.013450	-1.166120
Methane	-17.9 ^b	-40.533944	0.049028	-40.484916
Ethane	-20.1 ^c	-79.856553	0.079655	-79.776898
Propane	-25.0 ^c	-119.181091	0.109567	-119.071524
Butane	-30.1 ^c	-158.505503	0.139496	-158.366007
2-Methylpropane	-32.1 ^c	-158.506447	0.139016	-158.367431
Pentane	-35.1 ^d	-197.829819	0.169476	-197.660343
Hexane	-40.0 ^e	-237.154141	0.199420	-236.954721
Heptane	-44.9 ^e	-276.478465	0.229369	-276.249096
Octane	-49.8 ^e	-315.802791	0.259319	-315.543472
3-Ethylpentane	-45.3 ^e	-276.473335	0.229277	-276.244058
Cyclopentane	-18.3 ^f	-196.611646	0.147537	-196.464109
Cyclohexane	-29.4 ^g	-235.944826	0.177822	-235.767004
Cubane	148.7 ^h	-309.532746	0.139610	-309.393136
Adamantane	-32.0 ⁱ	-390.823729	0.252480	-390.571249
Benzene	19.8 ^j	-232.311249	0.106065	-232.205184
Methylbenzene	12.0 ^j	-271.638813	0.135478	-271.503335
2-Phenylpropane	0.9 ^j	-389.611763	0.225103	-389.386660
HCN	32.3 ^b	-93.454356	0.018585	-93.435771
(z)-Diazene (N ₂ H ₂)	50.9 ^b	-110.668976	0.031400	-110.637576
Ammonia	-11.0 ^b	-56.582484	0.038335	-56.544149
Methylamine	-5.6 ^k	-95.893694	0.068751	-95.824943
Dimethylamine	-4.7 ^l	-135.209520	0.098322	-135.111198
Pyrrolidine	-0.8 ^m	-212.646347	0.136150	-212.510197
Water	-57.8 ^b	-76.458420	0.024940	-76.433480
Ethanol	-56.2 ⁿ	-155.094900	0.085566	-155.009334
Ethylacetate	-106.5 ^o	-307.803953	0.127163	-307.676790
Formic acid	-90.5 ^p	-189.827624	0.038026	-189.789598
Nitric acid	-32.1 ^b	-280.978370	0.030917	-280.947453
Trinitromethane	-0.2 ^q	-654.163357	0.064715	-654.098642
1,1-Dinitroethane	-24.4 ^q	-488.966358	0.090205	-488.876153

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Table A-5. Electrostatic potential properties on single molecule
0.001 electrons/bohr³ surfaces as determined by
B3LYP/6-31G(d) calculations.

Compound	SA	σ^2	ν
Hydrogen azide	71.8	240.6	0.140
1-Azidobutane	161.4	66.4	0.194
1-Azidopentane	182.7	65.7	0.191
1-Azidohexane	203.9	69.8	0.181
1-Azidoheptane	225.1	71.7	0.174
1-Azidooctane	246.3	74.9	0.164
1,3-Diazidopropane	173.8	89.2	0.232
1,4-Diazidobutane	196.8	70.7	0.250
1,5-Diazidopentane	218.0	71.3	0.248
1,6-Diazidohexane	239.2	64.1	0.233
1,8-Diazidooctane	281.7	61.3	0.207
2-Azido-N-methylethanamine	154.9	79.0	0.201
2-Azido-N,N-dimethylethanamine	169.3	72.5	0.147
2-Azido-N-cyclopropylethanamine	185.3	69.6	0.223
1-(2-Azidoethyl)pyrrolidine	193.8	71.3	0.147
Bis(2-azidoethyl)methanamine	220.3	68.8	0.238
2-Azidoethanol	128.2	164.9	0.225
Azidotrinitromethane	171.9	100.3	0.097
1-Azido-1,1-dinitroethane	163.5	96.3	0.202
Azidobenzene	157.9	44.7	0.250
Azidomethylbenzene	179.5	66.0	0.232
Azidocyclohexane	176.1	63.0	0.128
Azidocyclopentane	161.7	65.7	0.161
3-Azidotriazole	133.5	399.8	0.248
4-Amino-3-azidotriazole	148.7	333.7	0.247
5-Methyl-3-azidotriazole	156.1	345.2	0.248
5-Methyl-4-amino-3-azidotriazole	169.3	324.9	0.237
5-Ethyl-3-azidotriazole	176.2	333.1	0.247
5-Ethyl-4-amino-3-azidotriazole	189.3	320.9	0.238
5-Phenyl-3-azidotriazole	215.6	256.4	0.250
5-Phenyl-4-amino-3-azidotriazole	226.5	254.9	0.250
4-Azidonitrobenzene	183.3	141.3	0.231

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